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Theory of incoherent spin dependent scattering of electrons at a disordered surface

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Abstract. A theoretical description of incoherent spin dependent multiple scattering of electrons at a single-crystal surface partially covered with a disordered overlayer is reported. A formalism in which occupation operators specify the occupancy of a chemisorption site is used for the statistical description of a disordered adlayer. The theory is based upon the concepts used in multiple-scattering DLEED theory. In the present considerations spin effects are introduced to this theory by using the time independent Dirac equation. Thus, a simple expression for incoherent spin dependent intensity is obtained. The spin–orbit induced 'up/down' asymmetry is then calculated. As an example the particular case of CO/Pt(111) is examined. It is found that diffuse SPLEED is sensitive to the geometrical parameters characterizing the substrate/disordered adsorbate system as well as to the parameters related to the statistical distribution of the occupied chemisorption sites. It is demonstrated that the method is applicable to any disordered surface suitable for DLEED investigation and in this way enlarges the number of experimental data convenient for disordered surface structure analysis.

1. Introduction

Experiments with low energy electron diffraction (LEED) are used for investigating the structures of the surface regions of pure crystals and of crystals covered with an adsorbate. The non-conventional use of the LEED technique provides information about the local atomic arrangement at disordered surfaces. In the mid-1980s, it was pointed out theoretically [1] that long-range order is not really essential. Diffuse LEED (DLEED) intensities carry information about the local adsorption structure. Different approaches have been proposed and put into practice to calculate the diffuse intensity distribution [2, 3]. One of the most general theoretical descriptions of coherent and incoherent multiple-scattering of electrons at a single-crystal surface partially covered with a disordered overlayer was presented by Le Bossé *et al* [4]. A general expression of the incoherent intensity (DLEED intensity) of electrons back-scattered at the substrate/disordered adsorbate system was given:

$$I_{incoh}(\vec{k}_f^- \leftarrow \vec{k}_i^+) = \frac{4\pi^4 k_i}{A k_{i\perp}} \sum_{p=1}^{p_{\max}} \sum_{p'=1}^{p_{\max}} \Gamma(p, p', \vec{k}_{f\parallel} - \vec{k}_{i\parallel}) \bar{K}_1(p, \vec{k}_f^- \leftarrow \vec{k}_i^+) K_1(p', \vec{k}_f^- \leftarrow \vec{k}_i^+). \tag{1.1}$$

It appears as a quadratic form in the $p_{\max}$ factors $K_1(p', \vec{k}_f^- \leftarrow \vec{k}_i^+)$, which are the effective amplitudes for the $p_{\max}$ possible occupancies of a chemisorption site (form factor). The matrix $\Gamma(p, p', \vec{k}_{f\parallel} - \vec{k}_{i\parallel})$, from which this quadratic form is derived, is nothing else than the Fourier transform on the lattice of the site occupancy pair correlation function for a pair of sites with

occupancies p and p' (structure factor). The evaluation of the site occupancy pair correlation function is obtained from the statistical mechanics treatment of chemisorbed layers in terms of lattice gas models. Three different methods were developed and tested [5, 6]. Two kinds of physical information are contained in the incoherent intensity: (1) the form factor contains information about the geometrical arrangement of elements which form the adsorbate p and about their position with respect to the substrate atoms and (2) the structure factor depends on the statistical distribution of adsorbate p at the 2D surface lattice site. In a DLEED experiment, the diffuse (incoherent diffraction) pattern is observed and the intensities of the scattered beams are recorded as functions of incident electron energy as well as scattering and incident electron directions. In order to find the local adsorption structure and the statistical distribution of the adsorbed elements (atoms or molecules), the calculated and measured DLEED intensities have to be compared by the best fit procedures.

The aim of this paper is to introduce the relativistic and polarization effects to the DLEED theory, which were successfully introduced into LEED theory making spin polarized LEED (SPLEED) [7] a very useful technique for surface structure analysis.

The electron–solid interaction Hamiltonian contains a spin dependent contribution; the diffracted beams exhibit, in addition to intensity variations, spin polarization effects, which can manifest themselves in two forms: (1) as an asymmetry in the scattered intensities for polarized incident beams of opposite spin alignment; (2) for an unpolarized incident beam, as spin polarization of the diffracted beams [8]. There are two types of spin dependent interaction mechanism relevant for LEED: (1) spin–orbit coupling and (2) the exchange interaction between the LEED electron and the ground state electrons, in the case of magnetic structures.

We focus, in this paper, on the non-magnetic cases. Polarization effects due to spin–orbit coupling were first predicted by Mott [9, 10] for large-angle elastic scattering of high-energy electrons by large-Z Coulomb potentials and experimentally confirmed by Shull *et al* [11]. Later on, they were also discovered in the scattering of slow electrons (a few eV to 1 keV) from Hg [8], W, Pt and Au [12] and noble gas atoms [13]. Spin polarization in LEED was qualitatively predicted by Maison [14], McRae [15] and Kessler [16]. Quantitative results obtained for W(001) by means of dynamical SPLEED theories [17, 18] corroborated these expectations and stimulated experimental work. Subsequent calculations for W(001) [19] and Au [20] gave encouraging agreement with the data and suggested a strong sensitivity of SPLEED to surface geometry. Since then, important advances have been made by a number of research groups [21, 22] and SPLEED has become one of the commonly used techniques for ordered surface structure analysis. Polarization and intensity studies naturally complement one another in that they depend in different ways on the scattering potential, and polarization profiles tend to emphasize regions of (E, Θ, φ) space where intensities are small.

In this paper, a relativistic theory of elastic back-scattering of polarized electrons at a disordered surface including multiple-scattering processes is introduced.

This theory is based upon the introduction of fieldlike operators which define the occupation of any chemisorption site of the substrate. According to the ideas of Lax [23] 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). The back-scattered intensities are the sum of a coherent part (the LEED intensity) and an incoherent part (DLEED intensity).

In the first stage the average of scattered wave fields has to be performed. For this purpose, the well known average t-matrix approximation (ATA) is used [4]. In the second stage the incoherent part of the wave scattered at the disordered overlayer is evaluated. It is assumed that this part depends linearly on the incoherent waves scattered at each site. This approximation

is totally impossible in the case of the coherent part because a relationship exists between the phases of coherent waves emitted at each site. It follows that these waves may strongly interfere in a constructive way. On the other hand, as the phases of the incoherent waves emitted at each site are random, these waves cannot interfere in a constructive way. Moreover, the fact that the disorder generally concerns the light chemisorbed atoms, which are also weak scatterers, is a further argument in favour of this approximation. Thanks to both mentioned approximations, it is possible to preserve the usual theoretical framework of LEED/SPLEED theory and so avoid a time-consuming cluster-like treatment of the problem.

The scheme of the present paper is of the following content.

- Section 2 contains all basic concepts used to construct spin dependent diffuse LEED theory (DSPLEED). A short outline of the statistical description of the disordered adlayer is presented in subsection 2.1. The general framework for the spin-polarized LEED calculations is given in subsection 2.2 while the basic ideas of diffuse LEED including spin are gathered in subsection 2.3.
- Section 3 is devoted to evaluation of the expression for the relativistic scattering amplitude in terms of occupation operators associated with a particular configuration of the adlayer.
- Section 4 deals with the expression of the relativistic scattering amplitude of the substrate in the presence of an overlayer in terms of the occupation operators (subsections 4.1 and 4.2) and is finished with the calculations of the spin dependent coherent and incoherent waves back-scattered by the substrate/disordered adsorbate system (subsections 4.3 and 4.4).
- Section 5 brings the numerically calculable expression for the spin dependent incoherent intensity of electrons back-scattered at the substrate/disordered adsorbate system.
- Section 6 collects the numerical results, which allows us to exemplify the discussed phenomena.
- Section 7 presents some final remarks.

2. Basic concepts

2.1. Outline of the statistical description of the disordered adlayer

The formalism in which occupation operators specify the occupancy of a chemisorption site was used in the DLEED theory [4]. The same concept will be applied in the present considerations (DSPLEED).

In general case, the model describing properties of an adsorbate layer is defined for the occupation operators $\sigma_i(p)$ which characterize state p of a site occupancy i of the surface lattice. One site can be occupied at most by one element. It is assumed that the surface coverage is smaller than unity. A configuration of the adlayer is defined by associating with each chemisorption site specified by the translation vectors T_i a vector $|p_i\rangle$ in which p_i can take a set of discrete values $0, 1, \ldots, p_{\max}$ corresponding to the different states of site i. It is assumed that $p_i = 0$ always represents the situation where site i is unoccupied. The other values of p_i can describe a large variety of situations such as (1) the chemisorption of one kind of atom ($p_i = p_{\max} = 1$ for an adatom on site i), (2) the coadsorption of two kinds of atom ($p_i = 1$ for an adatom A on site i and $p_i = p_{\max} = 2$ for an adatom B on site i), (3) the chemisorption of a molecule with two possible orientations ($p_i = 1$ for one orientation and $p_i = p_{\max} = 2$ for the other one) etc. A particular configuration of the adlayer is characterized by the state vector $|p_1, p_2, \ldots, p_N\rangle = |p_1\rangle \otimes |p_2\rangle \otimes \cdots \otimes |p_N\rangle$ in which N denotes the number of chemisorption sites of the surface. It is assumed that the set of these vectors generates an Euclidean vector space in which a scalar product is defined

by $\langle p_1, p_2, \ldots, p_N | p'_1, p'_2, \ldots, p'_N \rangle = \delta_{p_1 p'_1}, \delta_{p_2 p'_2}, \ldots, \delta_{p_N p'_N}$. The occupation operators $\sigma_i(p)$ are defined as $\sigma_i(p_i)|p_1, p_2, \ldots, p_N\rangle = \delta_{p_i p_i}|p_1, p_2, \ldots, p_N\rangle$. Since the sites must necessarily be in one of the $p_{\max} + 1$ states of occupancy, the σ values are interconnected by $\sum_{p=0}^{p_{\max}} \sigma_i(p) = 1$.

The statistical description of the adlayer requires the knowledge of a Hamiltonian which describes the interactions between adelements and between adsorbate and substrate. It is assumed that the interactions between adelements are described in terms of pair interactions Next, for each chemisorption state p the adsorption energy $E_{\text{ads}}(p)$ is defined. So, the Hamiltonian for the adsorbate plus substrate system takes the form

$$H = -\sum_{p_i}^{p_{\max}} \sum_{i=1}^{N} E_{\text{ads}}(p_i)\sigma_i(p_i) + \frac{1}{2} \sum_{p_i, p_1=1}^{p_{\max}} \sum_{i,j=1}^{N} U_{ij}(p_i p_j)\sigma_i(p_i)\sigma_j(p_j) \qquad (2.1)$$

which corresponds to a quadratic term describing an interaction between site i in state p_i and site j in state p_j with energy $U_{ij}(p_i p_j)$ and a linear term describing adsorbate substrate coupling. N is the number of all elements of the adlayer.

2.2. *Low-energy electron diffraction including spin*

In conventional (unpolarized or spin-averaged) LEED and DLEED, the maximum of information on the surface is obtained (1) by measuring the intensities I of diffracted beams as functions of energy E and wavevector $\vec{k}$ (which is usually characterized by polar angle of incidence θ with respect to the surface normal and by azimuthal angle φ) and (2) by comparing them to their theoretical counterparts calculated for the assumed surface structural models.

In SPLEED one extends the conventional approach either by a spin-polarized incident beam or by spin analysis of the diffracted beams, or, more ambitiously, by both.

In general case one has the basic observable quantities, the intensity $I(E, \theta, \varphi, P)$ and the polarization $P(E, \theta, \varphi, P)$. The spin effects in the scattering of spin-polarized low-energy electron diffraction by the surface manifest by reversal of the incident beam polarization as well as by reversal of the direction of surface magnetization. Thus, one has to distinguish for each diffracted beam four intensities I_s^m, where $s = (\uparrow\downarrow)$ refers to the directions of the incident beam polarization and $m = (\uparrow\downarrow)$ corresponds to the directions of the effective magnetic field parallel and antiparallel to the surface magnetization axis.

This four intensities I_s^m define three scattering asymmetries:

$$\begin{aligned} A_{so} &= (I_\uparrow^\downarrow + I_\uparrow^\downarrow - I_\downarrow^\uparrow - I_\downarrow^\downarrow)/I \\ A_{ex} &= (I_\uparrow^\uparrow + I_\downarrow^\downarrow - I_\downarrow^\uparrow - I_\uparrow^\downarrow)/I \\ A_u &= (I_\uparrow^\uparrow + I_\downarrow^\uparrow - I_\uparrow^\downarrow - I_\downarrow^\downarrow)/I. \end{aligned} \qquad (2.2)$$

The physical meaning of these asymmetries is indicated by the subscripts: 'so' for spin–orbit, 'ex' for exchange and 'u' for unpolarized. For non-magnetic materials, the only relevant spin dependent mechanism is spin–orbit coupling, and consequently $A_{ex} = A_u = 0$, leaving that

$$A_{so} = (I_\uparrow - I_\downarrow)/(I_\uparrow + I_\downarrow) \qquad (2.3)$$

which is the spin–orbit induced 'up/down' asymmetry coming from the fact that spin-up ($s = \uparrow$) and spin-down ($s = \downarrow$) electrons experience different effective scattering potentials due to the different sign of the spin–orbit coupling term [8].

The present paper is devoted to the non-magnetic materials case. Thus, spin–orbit coupling effects in the scattering of a polarized electron by a spherical symmetric potential V can be as usual fully obtained from the time independent Dirac equation [24]:

$$[-\alpha(\mathrm{i}\nabla) + \beta + eV(\vec{r})]\psi(\vec{r}) = E_0\psi(\vec{r}) \qquad (2.4)$$

where E_0 is the total energy of an electron, $\psi(r)$ is a four-component spinor and $e = -|e|$. α_k and β are (4×4) matrices which can be expressed in terms of the (2×2) Pauli matrices:

$$\rho_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \rho_2 = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} \qquad \rho_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

as the tensor products:

$$\beta = \rho \otimes I \qquad \alpha_k = \rho_1 \otimes \rho_k \qquad k = 1, 2, 3$$

$I \equiv \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ is the unity matrix.

Equation (2.4) represents a system of four simultaneous first-order partial equations which must be solved with an asymptotic form

$$\psi(\vec{r}) \underset{r\to\infty}{\longrightarrow} u_{\uparrow\downarrow} \exp(\mathrm{i}k\vec{r}) + f(\Theta)\frac{\exp(\mathrm{i}k\vec{r})}{r} \tag{2.5}$$

for the four components of the wave function $\psi(\vec{r})$. To solve the system of equations (2.4) with the boundary conditions (2.5) the Green function method is used. It allows us to write the system of the differential equations as the system of the integral equations:

$$\psi(\vec{r}) = u_{\uparrow\downarrow} \exp(\mathrm{i}k\vec{r}) + \int G(\vec{r}, \vec{r}')V(\vec{r}')\psi(\vec{r}')\,\mathrm{d}^3\vec{r}' \tag{2.6}$$

where $\varphi = u_{\uparrow\downarrow} \exp(\mathrm{i}kr)$ is the solution of the system of homogeneous differential equations

$$[-\alpha(\mathrm{i}\nabla) + \beta - E_0]\varphi = 0 \tag{2.7}$$

while the four-component spinor Green function $G(\vec{r}, \vec{r}')$ satisfies a system of equations:

$$[-\alpha(\mathrm{i}\nabla) + \beta - E_0]G(\vec{r}, \vec{r}') = \delta(\vec{r}, \vec{r}'). \tag{2.8}$$

From the above equations, SPLEED single-scattering results from a crystal consisting of identical atoms are easily obtained [24]. On the basis of the dynamical LEED theories [25], the dynamical SPLEED theory was also developed [7].

2.3. Diffuse low-energy electron diffraction including spin

On the basis of two previous subsections, the construction of the diffuse LEED theory including spin–orbit coupling is now presented. Theoretical description of spin dependent incoherent scattering of electrons at a single-crystal surface partially covered with a disordered overlayer is a main goal of this presentation.

Let us consider an electron of wavevector $\vec{k}$, moving towards a target consisting of the adlayer on the substrate. Its wave function Ψ_k (more especially the scattered part of this wave function) depends on the configuration $|p_1, p_2, \ldots, p_N\rangle$ of the target. So the measurement of a physical quantity A ascribed to the electron is the statistical average [4]

$$\langle A \rangle = \sum_{p_1=0}^{p_{\max}} \sum_{p_N=0}^{p_{\max}} \lambda(p_1, \ldots, p_N) A(p_1, \ldots, p_N)$$

in which the quantum average of A and the probability λ of finding the configuration state $|p_1, p_2, \ldots, p_N\rangle$ λ are respectively given by

$$A(p_1, \ldots, p_N) = \int \mathrm{d}\vec{r} \int \mathrm{d}\vec{r}'\psi(p_1, \ldots, p_N; \vec{r})A(\vec{r}, \vec{r}')\psi(p_1, \ldots, p_N; \vec{r}')$$

$$\lambda(p_1, \ldots, p_N) = \mathrm{tr}[\rho\sigma_1(p_1)\ldots\sigma_N(p_N)].$$

In these relations $A(\vec{r}, \vec{r}')$ is the $\vec{r}$-representation of the operator corresponding to the physical quantity A and ρ is the density matrix of the adlayer plus substrate system. Using the two last expressions $\langle A \rangle$ can be rewritten as

$$\langle A \rangle = \int \mathrm{d}\vec{r} \int \mathrm{d}\vec{r}' \, \mathrm{tr}[\rho \mathbf{\Psi}(\vec{r}) A(\vec{r}, \vec{r}') \mathbf{\Psi}(\vec{r}')]$$

where the fieldlike operator $\mathbf{\Psi}$ acting on states $|p_1, p_2, \ldots, p_N\rangle$ is given by

$$\mathbf{\Psi}(\vec{r}) = \sum_{p_1 \ldots p_N} \sigma_1(p_1) \ldots \sigma_N(p_N) \psi(p_1, \ldots, p_N; \vec{r}). \tag{2.9}$$

In order to separate incoherent scattering from diffraction $\mathbf{\Psi}(\vec{r})$ is decomposed into two parts:

$$\mathbf{\Psi}(\vec{r}) = \langle \Psi(\vec{r}) \rangle + \delta \mathbf{\Psi}(\vec{r}). \tag{2.10}$$

$\langle \Psi(\vec{r}) \rangle$ denotes the statistical average of the wave functions $\mathbf{\Psi}(p_1 \ldots p_N; \vec{r})$ and $\delta \mathbf{\Psi}(\vec{r})$ takes into account the fluctuations associated with the difference between the average configuration and the configurations of adelements actually 'seen' by incident electrons. It follows that $\langle \delta \mathbf{\Psi}(\vec{r}) \rangle = 0$.

It can be easily shown that $\langle A \rangle$ can be decomposed into

$$\langle A \rangle = \langle A \rangle_{coh} + \langle A \rangle_{incoh} \tag{2.11}$$

in which the coherent and incoherent parts of the average value of A are respectively given by

$$\langle A \rangle_{coh} = \int \mathrm{d}\vec{r} \int \mathrm{d}\vec{r}' \langle \mathbf{\Psi}(\vec{r}) \rangle A(\vec{r}, \vec{r}') \langle \mathbf{\Psi}(\vec{r}') \rangle$$

$$\langle A \rangle_{incoh} = \int \mathrm{d}\vec{r} \int \mathrm{d}\vec{r}' \, \mathrm{tr}[\rho \delta \mathbf{\Psi}(\vec{r}) A(\vec{r}, \vec{r}') \delta \mathbf{\Psi}(\vec{r}')].$$

The above construction is using the ideas applied in the case of the DLEED theory including multiple-scattering processes and based on the formalism in which occupation operators σ specify the occupancy of a chemisorption site [4]. In order to take into account the spin effects, the Dirac equation will be used instead of the Schrödinger equation. The differences resulting from employing the Dirac equation rather that the Schrödinger one show up in DLEED in two forms: first as intensity corrections and second as spin polarization or intensity asymmetry. The next sections will be devoted to the detailed description of the spin dependent DLEED theory.

3. Spin dependent scattering amplitude of the adlayer

3.1. Spin dependent scattering amplitude associated with a particular configuration of the adlayer

The relativistic scattering amplitude of the adlayer with a given arrangement of adelements will be now evaluated. Let us call $\vec{k}_i^n$ the wavevector of the electron incident on the adlayer. The superscript n is + or − according to whether the z component of the wavevector perpendicular to the surface is positive or negative. It is assumed that the incident electron is described by a Dirac plane wave of the form $u_{\uparrow\downarrow} \exp(\mathrm{i}\vec{k}_i \vec{r})$. Including incident and scattered waves the total wavefunction is given by

$$\psi(p_1, \ldots, p_N, \vec{r}) = u_{\uparrow\downarrow} \exp(\mathrm{i}\vec{k}_i^n \vec{r}) + \int \mathrm{d}\vec{k}_f^{n'} \langle \vec{k}_f^{n'} | G_0(E) T_{ad}(p_1, \ldots, p_N) | \vec{k}_i^n \rangle \exp(\mathrm{i}\vec{k}_f^{n'} \vec{r}) \tag{3.1}$$

in which $E = |\vec{k}_i^n|^2$ is the energy of the incident electron, $T_{ad}(p_1 \ldots p_N)$ is the relativistic transition matrix of the adlayer in the configuration state $|p_1, \ldots, p_N\rangle$ and $G_0(E)$ is the Green

operator of the Dirac free electron. $T_{ad}(p_1 \dots p_N)$ can be expressed in terms of the effective transition matrices t_i^* associated with each site i:

$$T_{ad}(p_1 \dots p_N) = \sum_{i=1}^{N} t_i^*. \tag{3.2}$$

These transition matrices provide the wave scattered at a site i in the presence of the other sites j and each of them is given by [4]

$$t_i^* = t_i(p_i) + t_i(p_i) G_0(E) \sum_{q \neq i} t_q^*. \tag{3.3}$$

The above relation shows that the effective transition matrix t_i^* is the sum of two terms: the first term $t_i(p_i)$ is the relativistic transition matrix of the isolated site i in the site occupancy p_i (this term is associated with a single scattering process at this site); the second term is more complicated and takes into account multiple-scattering processes. These processes take place when the scattering of an electron at site i is the last elementary process which follows the effective scattering at other sites. The transition matrix $t(0)$ of a vacancy is obviously zero. As a matter of fact, t_i^* depends on the set of parameters $(p_1, \dots, p_i, \dots, p_N)$. Nevertheless, in order to make the mathematical formalism lighter, writing down this dependence explicitly is omitted. Substituting expression (3.2) of the relativistic transition matrix T_{ad} in the total wavefunction defined by (3.1) and integrating over the z component of the wavevector by the method of contour integrals, one obtains

$$\begin{aligned}\psi(p_1, \dots p_N, \vec{r}) &= u_{\uparrow\downarrow} \exp(\mathrm{i}\vec{k}_i^n \vec{r}) \\ &\quad + \sum_{n'} \int \mathrm{d}k_{f\parallel} M^{\uparrow\downarrow}(p_1, \dots, p_N; \vec{k}_f^{n'} \leftarrow \vec{k}_i^n) \exp(\mathrm{i}\vec{k}_i^{n'} \vec{r}) \Theta(n'(z - R_\perp)).\end{aligned} \tag{3.4}$$

In this relation $R_\perp$ is the distance from the adelement plane to the origin of space, $\Theta(z)$ is the Heaviside distribution and the relativistic scattering amplitude of the adlayer is given by

$$M^{\uparrow\downarrow}(p_1, \dots, p_N; \vec{k}_f^{n'} \leftarrow \vec{k}_f^n) = \frac{-\mathrm{i}\pi}{k_{f\perp}} \exp(-\mathrm{i}\vec{k}_f^{n'} \vec{R}) \sum_{q=1}^{N} t_q^*(\vec{k}_f^{n'} \leftarrow \vec{k}_i^n) \exp(\mathrm{i}\vec{k}_i^n \vec{R}) \tag{3.5}$$

where $\vec{R}$ is the vector associated with the translation from the origin of space to the reference site of the adlayer.

3.2. Expression for the spin dependent scattering amplitude in terms of occupation operators σ

Now, we find relativistic scattering amplitude operators similar to the fieldlike operator $\mathbf{\Psi}(\vec{r})$ introduced in subsection 2.3. For this purpose, the expression (3.4) is substituted in the definition (2.9) and we obtain

$$\mathbf{\Psi}(\vec{r})^{\uparrow\downarrow} = u_{\uparrow\downarrow} \exp(\mathrm{i}\vec{k}_i^n \vec{r}) + \sum_{n'} \int \mathrm{d}k_{f\parallel} \mathbf{M}^{\uparrow\downarrow}(\vec{k}_f^{n'} \leftarrow \vec{k}_f^n) \exp(\mathrm{i}\vec{k}_f^{n'} \vec{r}) \Theta(n'(z - R_\perp)) \tag{3.6}$$

in which the matrix elements of $\mathbf{M}^{\uparrow\downarrow}$ are given by

$$\mathbf{M}^{\uparrow\downarrow}(\vec{k}_f^{n'} \leftarrow \vec{k}_f^n) = \frac{-\mathrm{i}\pi}{k_{f\perp}} \exp(-\mathrm{i}\vec{k}_f^{n'} \vec{R}) \sum_{q=1}^{N} \mathbf{T}_q^*(\vec{k}_f^{n'} \leftarrow \vec{k}_i^n) \exp(\mathrm{i}\vec{k}_i^n \vec{R}). \tag{3.7}$$

$\mathbf{\Psi}^{\uparrow\downarrow}$, $\mathbf{M}^{\uparrow\downarrow}$ and $\mathbf{T}_q^{\uparrow\downarrow}$ are operators acting in the configuration space. The latter operator is given by

$$\mathbf{T}_q^*(\vec{k}_f^{n'} \leftarrow \vec{k}_i^n) = \sum_{p_1 \cdots p_N} \sigma_1(p_1) \dots \sigma_N(p_N) t_q^*(\vec{k}_f^{n'} \leftarrow \vec{k}_i^n). \tag{3.8}$$

In subsequent developments, $\langle\mathbf{\Psi}\rangle^{\uparrow\downarrow}$ and $\delta\mathbf{\Psi}^{\uparrow\downarrow}$ will be expressed in terms of the effective scattering amplitudes of sites and of the factor characterizing the statistical distribution of adsorbed species. This requires the preliminary evaluation of $\langle\mathbf{M}^{\uparrow\downarrow}\rangle$ and $\delta\mathbf{M}^{\uparrow\downarrow}$ and consequently the evaluation of $\langle\mathbf{T}_q^*\rangle$ and $\delta\mathbf{T}_q^*$. It is not possible to obtain the exact expressions for these quantities. However, $\langle\mathbf{T}_q^*\rangle$ and $\delta\mathbf{T}_q^*$ can be determined by using well known approximations, presented later on in this section.

First, $\langle\mathbf{M}^{\uparrow\downarrow}\rangle$ will be calculated in terms of the average transition matrix of the reference site. The average transition matrix coefficient $\langle\mathbf{T}_q^*(\vec{k}_f^{n'} \leftarrow \vec{k}_i^n)\rangle$ at site q and the similar quantity at site 1 differ by a simple phase factor. This translation property is due to the fact that all sites are statistically equivalent. Thus, any average quantity ascribed to a site verifies such a property. In particular we can write

$$\langle\mathbf{T}_q^*(\vec{k}_f^{n'} \leftarrow \vec{k}_i^n)\rangle = \exp\lfloor -\mathrm{i}(\vec{k}_f^{n'} \leftarrow \vec{k}_i^n)(\vec{T}_q - \vec{T}_q)\rfloor\langle\mathbf{T}_1^*(\vec{k}_f^{n'} \leftarrow \vec{k}_i^n)\rangle \tag{3.9}$$

where the 2D lattice vector $\vec{T}_q - \vec{T}_1$ defines the position of site q relative to site 1 considered as the reference site.

The relation (3.9) is now used to express the average of quantity $\mathbf{M}^{\uparrow\downarrow}$ given by the relation (3.7):

$$\langle\mathbf{M}^{\uparrow\downarrow}(\vec{k}_f^{n'} \leftarrow \vec{k}_f^n)\rangle \frac{-4\mathrm{i}\pi^3}{Ak_{g\perp}} \sum_{\{g\}} \exp(-\mathrm{i}\vec{k}_{ig}^{n'}\vec{R})\langle\mathbf{T}_1^*(\vec{k}_{ig}^{n'} \leftarrow \vec{k}_i^n)\rangle \exp(-\mathrm{i}\vec{k}_i^n\vec{R})\delta(\vec{k}_{f\parallel} - \vec{k}_{i\parallel} - \vec{g}). \tag{3.10}$$

The above expression was obtained with the help of the well known summation relation:

$$\sum_{q=1}^{N} \exp[-\mathrm{i}(\vec{k}_f^{n'} \leftarrow \vec{k}_i^n)(\vec{T}_q - \vec{T}_1)] = \frac{\pi^2}{A}\sum_{\{g\}} \delta(\vec{k}_{f\parallel} - \vec{k}_{i\parallel} - \vec{g}). \tag{3.11}$$

A occurring in (3.10) and (3.11) is the area of the unit cell of the 2D lattice while $\{g\}$ denotes the set of reciprocal lattice vectors and $\vec{k}_{ig}^{n'}$ is given by:

$$\vec{k}_{ig}^{n'} = \vec{k}_{i\parallel} + \vec{g} + n'\vec{u}_z k_{ig\perp} \qquad k_{ig\perp} = (E - |\vec{k}_{i\parallel} + \vec{g}|^2)^{1/2}$$

where $\vec{u}_z$ is a unit vector in the z direction.

The relation (3.10) clearly indicates that the average amplitude matrix $\langle\mathbf{M}^{\uparrow\downarrow}\rangle$ takes into account the electron diffraction by a 2D lattice of mean adscatterers.

3.3. Calculation of $\langle\mathbf{M}^{\uparrow\downarrow}(\vec{k}_f^{n'} \leftarrow \vec{k}_i^n)\rangle$

We have seen that the average of the adlayer amplitude matrix $\langle\mathbf{M}^{\uparrow\downarrow}\rangle$ can be expressed in terms of the average of the reference-site transition matrix. Thus, we should evaluate it. For this purpose the approximations successfully applied in the case of general DLEED calculations [4] will be used. Making use of the properties of σ (subsection 2.1), it can be easily seen that $\mathbf{T}_1^*$ satisfies the following equation:

$$\mathbf{T}_1^* = \mathbf{T}_1 + \mathbf{T}_1 G_0(E)\sum_{q\neq 1}\mathbf{T}_q^* \tag{3.12}$$

where $\mathbf{T}_1 = \sum_{p=1}^{p_{\max}} \sigma_1(p)t_1(p)$.

Looking at equation (3.12), the possible approximation is to replace the operators $\mathbf{T}_q^*$ with their average performed over the whole statistical ensemble. Within this mean-field-like approximation, the last scattering process occurring at site 1 is rigorously described while the previous scattering processes occurring at other sites are approximated by their average. In order to take into account the correlations between the occupancies of two adsorption sits in

a adlayer, a modified mean-field-like approximation will be applied [4]. The average transition matrix obtained in this approximation satisfies the following equation:

$$\langle \mathbf{T}_1^* \rangle = \langle \mathbf{T}_1 \rangle \left(1 + G_0(E) \sum_{q \neq 1} \langle \mathbf{T}_q^* \rangle_1^p \right). \tag{3.13}$$

This relation corresponds to the modified average transition-matrix approximation (ATA) used in DLEED [4] theory. The quantity $\langle \mathbf{T}_q^* \rangle_1^p$ occurring in relation (3.13) is given by

$$\langle \mathbf{T}_q^* \rangle_1^p = \frac{\langle \sigma_1(p) \mathbf{T}_1^* \rangle}{\langle \sigma_1(p) \rangle}$$

and represents the average of $\mathbf{T}_q^*$ performed over a set of configurations in which the reference site 1 is in the fixed occupancy state p. If there is no correlation between the scattered wave amplitude at site 1 and the occupancy of site q, the average $\langle \mathbf{T}_q^* \rangle_1^p$ can be replaced with average $\langle \mathbf{T}_q^* \rangle$ performed over the whole statistical ensemble. In this way we come back to the well known ATA widely used in the LEED theory [26]. Obviously, this replacement is valid only in the case of a totally random adlayer. Unfortunately, such a situation is rarely found. In most cases, partially ordered phase exist. Thus, it will be necessary to consider mean-field-like approximations for which correlation between pairs, and higher conformations are taken into account [4].

Using the expansion of a plane wave on the basis of the set of spherical waves [7] in the presence of spin–orbit coupling it can be easily shown that:

$$\begin{aligned} \langle \mathbf{T}_1^*(\vec{k}_f^{n'} \leftarrow \vec{k}_i^n) \rangle = \frac{2}{\pi} \sum_{\kappa\mu,\kappa'\mu'} & C(l\tfrac{1}{2}j; \mu - s', s') Y^*_{l\mu-s'}(\vec{k}_f^{n'}) \langle \mathbf{T}_1^*(\kappa\mu, \kappa'\mu') \rangle \\ & \times C(l\tfrac{1}{2}j; \mu - s, s) Y^*_{l\mu-x}(\vec{k}_l^n) \end{aligned} \tag{3.14}$$

where the fact that the non-magnetic systems are considered were taken into account. $Y_L(\vec{k})$ denotes the usual spherical harmonics. The Clebsh–Gordan coefficients $C(l\frac{1}{2}j, \mu - s, s)$ are defined by [24]:

$$\begin{aligned} & \left[\frac{l + (s/|s|)\mu + \frac{1}{2}}{2l+1} \right]^{1/2} && \text{for } j = l + \frac{1}{2} \ (\kappa = -l - 1) \\ & -\frac{s}{|s|} \left[\frac{l - (s/|s|)\mu + \frac{1}{2}}{2l+1} \right]^{1/2} && \text{for } j = l - \frac{1}{2} \ (\kappa = l). \end{aligned}$$

Then, from equation (3.13), it follows that

$$\begin{aligned} \langle \mathbf{T}_1^*(\kappa\mu, \kappa'\mu') \rangle = & \langle \mathbf{T}_1(\kappa\mu, \kappa'\mu') \rangle \\ & + \sum_{\kappa''\mu'',\kappa'''\mu'''} \langle \mathbf{T}_1(\kappa\mu, \kappa''\mu'') \rangle G(\kappa''\mu'', \kappa'''\mu''') \langle \mathbf{T}_1(\kappa'''\mu''', \kappa'\mu') \rangle. \end{aligned} \tag{3.15}$$

Using equation (3.15), we obtain the relation

$$\langle \mathbf{T}_1^*(\kappa\mu, \kappa'\mu') \rangle = [(1 - X)^{-1} \langle \mathbf{T}_1 \rangle]_{\kappa\mu,\kappa'\mu'} \tag{3.16}$$

in which the elements of the scattering matrix X are given by

$$\begin{aligned} X_{\kappa\mu,\kappa'\mu'} = \langle \mathbf{T}_1 \rangle & \sum_{s=\pm\frac{1}{2}} C(l\tfrac{1}{2}j, \mu \mp \tfrac{1}{2}, \pm\tfrac{1}{2}) C(l'\tfrac{1}{2}j', \mu' - s, s) \\ & \times \sum_m \exp(\mathrm{i}\vec{k}_{i\parallel} \vec{R}_m) G_{l,\mu\mu 1/2; l',\mu'-s}(\vec{R} - \vec{R}_m) \end{aligned} \tag{3.17}$$

where the lattice summation remains the same as in the spinless case while the dimension of X is doubled to $2(l_{\max}+1)^2\,2(l_{\max}+1)^2$, where $l_{\max} = \sup(l)$ is taken into account. The Green function is determined due to the definition given by Pendry [25]:

$$G_{lm''m''}(\vec{R}-\vec{R}_m) = \sum_{l'm'} 4\pi(-1)^{1/2(l-l'-l'')}(-1)^{m'+m''}B^l(l'm',l''m'')D_{l'm'} \tag{3.18}$$

where $B^l(l'm',l''m'')$ are the Gaunt coefficients and $D_{l'm'}$ are the structure factors.

The evaluation of the Green function operators is based on the Kambe's method used in LEED theory [25] and SPLEED theory [7] as well as in DLEED theory [4].

The average value $\langle \mathbf{T}_1\rangle$ can be rewritten in the form

$$\langle \mathbf{T}_1\rangle = \sum_{p=1}^{p_{\max}} \langle\sigma_1(p)\rangle t_1(p). \tag{3.19}$$

Finally, from equations (3.10), (3.14) and (3.16) a well known expression for $\langle \mathbf{M}^{\uparrow\downarrow}\rangle$ is obtained, i.e.

$$\begin{aligned}\langle \mathbf{M}^{\uparrow\downarrow}(\vec{k}_f^{n'} \leftarrow \vec{k}_i^n)\rangle = {} & \frac{-8\mathrm{i}\pi^2}{Ak_{g\perp}} \sum_{\{g\}} \exp(-\mathrm{i}\vec{k}_{ig}^{n'}\vec{R}) \\ & \times \sum_{\kappa\mu\kappa'\mu'} C(l\tfrac{1}{2}j,\mu\mp\tfrac{1}{2},\pm\tfrac{1}{2})Y^*_{l,\mu\mu 1/2}(\vec{k}_{ig}^{n'})[(1-X)^{-1}\langle\mathbf{T}_1\rangle]_{\kappa\mu\kappa'\mu'} \\ & \times \sum_{s=\pm 1/2} C(l\tfrac{1}{2}j,\mu-s,s)Y_{l,\mu-s}(\vec{k}_i^n)\exp(-\mathrm{i}\vec{k}_i^n\vec{R})\delta(\vec{k}_{f\parallel}-\vec{k}_{i\parallel}-g)\end{aligned} \tag{3.20}$$

where the summation over κ corresponds to the summation over two configurations: $\kappa = -l-1$ for $j = l+\frac{1}{2}$ and $\kappa = l$ for $j = l-\frac{1}{2}$ (cf the definition of the Clebsh–Gordan coefficients).

Thus, the fact that the spin effects were taken into account in the calculation of the coherent part of the adlayer amplitude matrix means it has the same form as in the case of elastic spin-polarized LEED from a crystalline surface [7]. The only difference arises from the fact that in the present case the coherent scattering process is dealing with a mean scatterer located at the reference site while in the case of SPLEED the transition matrix is not averaged.

3.4. Calculation of $\delta\mathbf{M}^{\uparrow\downarrow}(\vec{k}_f^{n'} \leftarrow \vec{k}_f^n)$

$\delta\mathbf{\Psi}^{\uparrow\downarrow}$ represents the electron wave function fluctuations coming from the differences between the actual adlayer configurations 'seen' by incident electrons and the average adlayer configuration:

$$\delta\mathbf{\Psi}^{\uparrow\downarrow} = \mu_{\uparrow\downarrow}\exp(\mathrm{i}\vec{k}_i^{n'}\vec{r}) + \sum_{n'} \mathrm{d}k_{f\parallel}\delta\mathbf{M}^{\uparrow\downarrow}\exp(\mathrm{i}\vec{k}_f^{n'}\vec{r})\Theta(n'(z-R_\perp)). \tag{3.21}$$

The fluctuations of the scattering matrix $\mathbf{M}^{\uparrow\downarrow}$ can be defined as follows:

$$\delta\mathbf{M}^{\uparrow\downarrow}(\vec{k}_f^{n'} \leftarrow \vec{k}_i^n) = \frac{-\mathrm{i}\pi}{k_{f\perp}}\exp(-\mathrm{i}\vec{k}_f^{n'}\vec{R})\sum_{i=1}^{N}\delta\mathbf{T}_i^*(\vec{k}_f^{n'} \leftarrow \vec{k}_i^n)\exp(\mathrm{i}\vec{k}_i^n\vec{R}). \tag{3.22}$$

By using the mean-field approximation introduced in subsection 3.3, it is easy to show that $\delta\mathbf{T}_i^*$ is given by [4]:

$$\delta\mathbf{T}^* = \delta\mathbf{T}\left(1 + G(E)\sum_{q\neq i}\langle\delta\mathbf{T}_q^*\rangle\right). \tag{3.23}$$

In this expression $\delta\mathbf{T}_i$ is defined as

$$\delta\mathbf{T}_i = \sum_{p=1}^{p_{\max}} [\sigma_i(p) - \langle\sigma_i(p)\rangle] t_i(p) \tag{3.24}$$

which is introduced in the way usually applied in the DLEED theory [4].

The expression for $\delta\mathbf{T}_i^*$ can be rewritten in a similar form:

$$\delta\mathbf{T}_i^* = \sum_{p=1}^{p_{\max}} [\sigma_i(p) - \langle\sigma_i(p)\rangle] I_i(p) \tag{3.25}$$

in which $t_i(p)$ is replaced by $I_i(p)$ given in the form

$$I_i(p) = t_i(p)\left(1 + G(E)\sum_{q\neq i}\langle\mathbf{T}_q^*\rangle\right) \tag{3.26}$$

on the basis of equations (3.23) and (3.24).

The expression (3.22) indicates that the calculations of $\delta\mathbf{M}^{\uparrow\downarrow}$ require preliminary evaluation of the matrix elements of $\delta\mathbf{T}_i^*$ in the momentum representation and next, according to (3.25), the evaluation of the matrix elements of $I_i(p)$. It is easily seen that $I_i(p)$ as well as $t_i(p)$ satisfies a translation property similar to (3.9) and one can express the matrix elements $I_i(p)$ in terms of the matrix of the reference site 1 in the basis of free spherical waves as a relation similar to (3.14):

$$\begin{aligned} I_i(p, \vec{k}_f^{n'} \leftarrow \vec{k}_i^n) = \frac{2}{\pi} \sum_{k\mu k'\mu'} & C(l\tfrac{1}{2}j, \mu - s', s') Y^*_{l,\mu-s'}(\vec{k}_f^{n'}) I_1(p, \kappa\mu, \kappa'\mu') \\ & \times C(l\tfrac{1}{2}j, \mu - s, s) Y_{l,\mu-s}(\vec{k}_i^n). \end{aligned} \tag{3.27}$$

Consequently:

$$I_1(p, \kappa\mu, \kappa'\mu') = [t_1(p)(1 - Z)^{-1}]_{\kappa\mu\kappa'\mu'} \tag{3.28}$$

where matrix elements of Z are given by

$$\begin{aligned} Z_{k\mu k'\mu'} = \sum_{s=\pm 1/2} & C(l\tfrac{1}{2}j, \mu \mp \tfrac{1}{2}, \pm\tfrac{1}{2}) C(l'\tfrac{1}{2}j', \mu' - s, s) \\ & \times \sum_m \exp(\mathrm{i}\vec{k}_{i\parallel}\vec{R}_m) G_{l,\mu\mu 1/2, l', \mu' - s}(\vec{R} - \vec{R}_m)\langle\mathbf{T}_1^*\rangle. \end{aligned} \tag{3.29}$$

Now, it is possible to give an expression for the scattering amplitude deviation in the momentum representation:

$$\delta\mathbf{M}^{\uparrow\downarrow}(\vec{k}_f^{n'} \leftarrow \vec{k}_i^n) = \frac{-\mathrm{i}\pi}{k_{f\perp}} \exp(-\mathrm{i}\vec{k}_f^{n'}\vec{R}) \sum_{i=1}^{p_{\max}} S(p, \vec{k}_f^{n'} \leftarrow \vec{k}_i^n) I_1(p, \vec{k}_f^{n'} \leftarrow \vec{k}_i^n) \exp(\mathrm{i}\vec{k}_i^n\vec{R}) \tag{3.30}$$

in which

$$S(p, \vec{k}_f^{n'} \leftarrow \vec{k}_i^n) = \sum_{i=1}^{N} [\sigma_i(p) - \langle\sigma_i(p)\rangle] \exp[-\mathrm{i}(\vec{k}_f^{n'} \leftarrow \vec{k}_i^n)(\vec{T}_i - \vec{T}_1)]. \tag{3.31}$$

The set of operators $\sigma_i(p)$ can be regarded as a discrete field which defines the chemical composition of the 2D lattice sites. Then, $\sigma_i(p) - \langle\sigma_i(p)\rangle$ is the deviation of this field from its average and $S(p, \vec{k}_f^{n'} \leftarrow \vec{k}_l^n)$ is the Fourier transform on the lattice of this deviation. Finally $\delta\mathbf{M}^{\uparrow\downarrow}$ is expressed in terms of a product of two factors: the first factor $S(p, \vec{k}_f^{n'} \leftarrow \vec{k}_i^n)$ characterizes the statistical distribution of elements in the adlayer; the second factor $I_1(p, \vec{k}_f^{n'} \leftarrow \vec{k}_i^n)$ characterizes their spin dependent scattering properties in the presence of the other adscatterers.

4. Spin dependent scattering amplitude of a disordered layer of elements adsorbed on a clean single-crystal surface

4.1. Spin dependent scattering amplitude associated with a particular configuration

The scattering amplitude of a single-crystal surface covered with a layer of chemisorbed elements is given by the well known relation:

$$\begin{aligned} A^{\uparrow\downarrow}(p_1,\ldots,p_N;\vec{k}_f^- \leftarrow \vec{k}_i^+) &= M^{\uparrow\downarrow}(p_1,\ldots,p_N;\vec{k}_f^- \leftarrow \vec{k}_i^+) \\ &\quad +[1+M^{\uparrow\downarrow}(p_1,\ldots,p_N;\vec{k}_f^- \leftarrow \vec{k}_i^-)] \\ &\quad \times[1-M_s^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^+)M^{\uparrow\downarrow}(p_1,\ldots,p_N;\vec{k}_f^+ \leftarrow \vec{k}_i^-)]^{-1}M_s^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^+) \\ &\quad \times[1+M^{\uparrow\downarrow}(p_1,\ldots,p_N;\vec{k}_f^+ \leftarrow \vec{k}_i^-)]. \end{aligned} \tag{4.1}$$

As the substrate surface is assumed to have a perfect 2D translation symmetry, we can assert that the momentum representation of the substrate back-scattering amplitude is a square matrix whose coefficients are given by

$$M_s^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^+) = \sum_{\{g\}} M_s^{\uparrow\downarrow}(\vec{k}_{ig}^- \leftarrow \vec{k}_i^+)\delta(\vec{k}_{f\parallel} \leftarrow \vec{k}_{i\parallel} - \vec{g}). \tag{4.2}$$

The definition of $M_s^{\uparrow\downarrow}$ implies that electrons reflected at the substrate surface move in the opposite direction to the z-axis and thus the metal is located in the region $z > 0$. In contrast to the substrate, the disordered adlayer has no 2D symmetry. It follows that an electron interacting with the adlayer may be scattered in any direction of space. As a mathematical consequence of this disorder, the scattering amplitude $M^{\uparrow\downarrow}(p_1,\ldots,p_N;\vec{k}_f^{n'} \leftarrow \vec{k}_i^n)$ is an integral operator with a kernel given by (3.5).

4.2. Spin dependent scattering amplitude of the substrate in the presence of an overlayer in terms of occupation operators σ

In the same way as $\mathbf{T}_i^*$ was defined in terms of t_i^* (see 3.8), we determine $\mathbf{A}^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^+)$ in terms of $A^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^+)$ by the relation

$$\mathbf{A}^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^+) = \sum_{p_1,\ldots,p_N} \sigma_1(p_1)\ldots\sigma_N(p_N)A^{\uparrow\downarrow}(p_1,\ldots,p_N;\vec{k}_f^- \leftarrow \vec{k}_i^+). \tag{4.3}$$

Taking into account the properties of the σ (see subsection 2.1) and the expansion of $A^{\uparrow\downarrow}(p_1,\ldots,p_N;\vec{k}_f^- \leftarrow \vec{k}_i^+)$ in a power series in $M_s^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^+)M^{\uparrow\downarrow}(p_1,\ldots,p_N;\vec{k}_f^+ \leftarrow \vec{k}_i^-)$ we can see that $\mathbf{A}^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^-)$ can be expressed by the relation

$$\begin{aligned} \mathbf{A}^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^+) &= \mathbf{M}^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^+) \\ &\quad +[1+\mathbf{M}^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^-)][1-M_s^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^+)\mathbf{M}^{\uparrow\downarrow}(\vec{k}_f^+ \leftarrow \vec{k}_i^-)]^{-1} \\ &\quad \times[M_s^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^+)(1+\mathbf{M}^{\uparrow\downarrow}(\vec{k}_f^+ \leftarrow \vec{k}_i^-))] \end{aligned} \tag{4.4}$$

similar to (4.1).

Now, in this relation the separation of $\mathbf{M}^{\uparrow\downarrow}(\vec{k}_f^{n'} \leftarrow \vec{k}_i^n)$ into the sum of its average $\langle\mathbf{M}^{\uparrow\downarrow}(\vec{k}_f^{n'} \leftarrow \vec{k}_i^n)\rangle$ and the deviation from this average $\delta\mathbf{M}^{\uparrow\downarrow}(\vec{k}_f^{n'} \leftarrow \vec{k}_i^n)$ will be done. Then, $\mathbf{A}^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^+)$ can be expanded in a power series in $\delta\mathbf{M}^{\uparrow\downarrow}(\vec{k}_f^{n'} \leftarrow \vec{k}_i^n)$ and the only terms kept will be those of zero and first order. This approximation consist in the assumption that the fluctuations of the scattering amplitude due to disorder are small when compared with

the coherent scattering amplitude. The same approximation was used in the general DLEED theory [4] and now it yields

$$\mathbf{A}^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^+) = \langle \mathbf{A}^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^+)\rangle + \delta\mathbf{A}^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^+) \tag{4.5}$$

in which $\langle \mathbf{A}^{\uparrow\downarrow}\rangle$ obeys the same equation as $A^{\uparrow\downarrow}$ in relation (4.4), i.e.

$$\begin{aligned}\langle \mathbf{A}^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^+)\rangle = {} & \langle \mathbf{M}^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^+) \\ & +[1 + \langle \mathbf{M}^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^-)][1 - M_s^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^+)\langle \mathbf{M}^{\uparrow\downarrow}(\vec{k}_f^+ \leftarrow \vec{k}_i^-)\rangle]^{-1} \\ & \times M_s^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^+)[1 + \langle \mathbf{M}^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^-)\rangle].\end{aligned} \tag{4.6}$$

It should be pointed out that similarly to the general DLEED theory [4], the applied set of approximations would be inconsistent with taking into account the multiple incoherent scattering processes while the equation (4.6) is kept. Thus, the fluctuations of $\mathbf{A}^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^+)$ are given by

$$\begin{aligned}\delta\mathbf{A}^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^+) = {} & \delta\mathbf{M}^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^+) + \delta\mathbf{M}^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^-)F_2 + F_1\delta\mathbf{M}^{\uparrow\downarrow}(\vec{k}_f^+ \leftarrow \vec{k}_i^+) \\ & +F_1\delta\mathbf{M}^{\uparrow\downarrow}(\vec{k}_f^+ \leftarrow \vec{k}_i^-)F_2\end{aligned} \tag{4.7}$$

in which:

$$F_1^{\uparrow\downarrow} = (1 + \langle \mathbf{M}^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^-)\rangle)[1 - M_s^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^+)\langle \mathbf{M}^{\uparrow\downarrow}(\vec{k}_f^+ \leftarrow \vec{k}_i^-)\rangle]^{-1}M_s^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^+)$$
$$F_2^{\uparrow\downarrow} = (1 - M_s^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^+)\langle \mathbf{M}^{\uparrow\downarrow}(\vec{k}_f^+ \leftarrow \vec{k}_i^-)\rangle)^{-1}M_s^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^+)(1 + \langle \mathbf{M}^{\uparrow\downarrow}(\vec{k}_f^+ \leftarrow \vec{k}_i^+)\rangle).$$

The four terms in expression (4.7) can be interpreted in the same way as in the case of general DLEED [4]. The first term is associated with a single backward incoherent scattering event at the adlayer. The second term takes into account processes in which a single forward incoherent event from the substrate through the adsorbate to the vacuum takes place after multiple coherent reflections between adlayer and substrate. The third term is associated with processes in which a single forward incoherent scattering event from the vacuum through the adsorbate to the substrate takes place before multiple coherent reflections between adlayer and substrate. The fourth term describes processes in which a single backward incoherent scattering occurs between multiple coherent reflections between adlayer and substrate.

4.3. Calculations of the spin dependent coherent wave $\langle\Psi(\vec{r})\rangle^{\uparrow\downarrow}$

Equation (4.6) indicates that the spin dependent coherent wave calculations require knowledge of the substrate back-scattering matrix $M_s^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^+)$. Its evaluation is related to the standard SPLEED technique and can be found in the books about SPLEED theory [21]. The total spin dependent coherent wave back-scattered at the surface of the adsorbate plus substrate system is given by

$$\langle\Psi(\vec{r})\rangle^{\uparrow\downarrow} = u_{\uparrow\downarrow}\exp(\mathrm{i}\vec{k}_i^+\vec{r}) + \sum_{\{g\}}\langle \mathbf{A}^{\uparrow\downarrow}(\vec{k}_{ig}^- \leftarrow \vec{k}_i^+)\rangle\exp(\mathrm{i}\vec{k}_{ig}^-\vec{r}) \tag{4.8}$$

where the average relativistic scattering matrix $\mathbf{A}^{\uparrow\downarrow}(\vec{k}_{ig}^- \leftarrow \vec{k}_i^+)$ is obtained from the relation (4.6). This expression is a linear combination of a few plane waves each of them being labelled with reciprocal lattice vector $\vec{g}$. The summation is restricted to these vectors $\vec{g}$ for which the component of $\vec{k}_{ig}^-$ perpendicular to the surface is real.

4.4. Calculation of the spin dependent incoherent wave $\delta\Psi(\vec{r})^{\uparrow\downarrow}$

The deviation of the scattered wave is given by

$$\delta\Psi(\vec{r})^{\uparrow\downarrow} = \int \mathrm{d}k_{f\parallel} \exp(-\mathrm{i}\vec{k}_f^- \vec{R})\delta\mathbf{A}^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^+) \exp(\mathrm{i}\vec{k}_i^+ \vec{R}) \exp(\mathrm{i}\vec{k}_f^- \vec{r}) \tag{4.9}$$

where $\delta\mathbf{A}^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^+)$ can be written in a simple form by using the relation (4.7) and (3.30):

$$\delta\mathbf{A}^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^+) = \frac{-\mathrm{i}\pi}{k_{f\perp}} \sum_{p=1}^{p_{\max}} S(p, \vec{k}_f^- \leftarrow \vec{k}_i^+) K_1^{\uparrow\downarrow}(p, \vec{k}_f^- \leftarrow \vec{k}_i^+) \tag{4.10}$$

in which

$$\begin{aligned} K_1^{\uparrow\downarrow} = {} & I_1(p, \vec{k}_f^- \leftarrow \vec{k}_i^+) + \sum_{\{g_1\}} I_1(p, \vec{k}_f^- \leftarrow \vec{k}_{ig_1}^-) F_2^{\uparrow\downarrow}(p, \vec{k}_{ig_1}^- \leftarrow \vec{k}_i^+) \\ & + \sum_{\{g_2\}} \frac{k_{f\perp}}{k_{fg_\perp}} F_1^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_{fg_2}^+) I_1(p, \vec{k}_{fg_2}^+ \leftarrow \vec{k}_i^+) \\ & + \sum_{\{g_1\}} \sum_{\{g_2\}} \frac{k_{f\perp}}{k_{fg_2\perp}} F_1^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_{fg_2}^+) I_1(p, \vec{k}_{fg_2}^+ \leftarrow \vec{k}_{ig_1}^-) F_2^{\uparrow\downarrow}(\vec{k}_{ig_1}^- \leftarrow \vec{k}_i^+). \end{aligned} \tag{4.11}$$

This relation can be interpreted in the same way as (4.7) under the condition that the adlayer is replaced with a single adscatterer located at the reference site 1. Thus, the deviation $\delta\mathbf{A}^{\uparrow\downarrow}(\vec{k}_f^- \leftarrow \vec{k}_i^+)$ of the relativistic scattering amplitude can be written as a product of two factors: $S(p, \vec{k}_f^- \leftarrow \vec{k}_i^+)$ which describes the statistical distribution of adscatterers around the reference site with occupancy p, and $K_1^{\uparrow\downarrow}(p, \vec{k}_f^- \leftarrow \vec{k}_i^+)$ which describes the incoherent scattering at this site in the presence of other adscatterers and of the substrate surface. It is worthwhile to notice that in contrast to the case of the coherent wave, the expression (4.9) for the incoherent wave is an integral over $k_{f\parallel}$ for any direction of space provided that the component $k_{f\perp}$ is real.

5. Spin dependent coherent and incoherent back-scattered intensities

Now, following the evaluation of general DLEED theory [4], the decomposition (2.10) of the average of an observable A can be applied to the particular case where A is the electron probability current density at $\vec{r}_0$. It is given by an expression in the following form:

$$\langle J(\vec{r}_0)\rangle = \langle J(\vec{r}_0)\rangle_{coh} + \langle J(\vec{r}_0)\rangle_{incoh} \tag{5.1}$$

in which

$$\langle J(\vec{r}_0)\rangle_{coh} = 2\,\mathrm{Im}\,\lfloor\langle\bar{\Psi}(\vec{r}_0)\rangle^{\uparrow\downarrow}\nabla\langle\Psi(\vec{r}_0)\rangle^{\uparrow\downarrow}\rfloor \tag{5.2}$$

$$\langle J(\vec{r}_0)\rangle_{incoh} = 2\,\mathrm{Im}\ \mathrm{tr}\lfloor\rho\delta\Psi(\vec{r}_0)\rangle^{\uparrow\downarrow}\nabla\delta\Psi(\vec{r}_0)\rangle^{\uparrow\downarrow}\rfloor. \tag{5.3}$$

We can see that the coherent part of the current is determined by the statistical averages of the wave function $\Psi(\vec{r}_0)^{\uparrow\downarrow}$ while the incoherent part is described by the fluctuations and corresponds to the diffuse SPLEED which is a subject of the present considerations.

5.1. Spin dependent coherent back-scattered intensity

From the relation (5.2) and (4.8), the flux of coherent back-scattered electrons per unit of surface and per unit of incident flux can be calculated. This calculation yields

$$I_{coh}^{\uparrow\downarrow} = \sum_{\{g\}} \frac{k_{ig\perp}}{k_{i\perp}} |\langle\mathbf{A}^{\uparrow\downarrow}(\vec{k}_{ig}^- \leftarrow \vec{k}_i^+)\rangle|^2. \tag{5.4}$$

The summation over $\vec{g}$ is performed over all the reciprocal lattice vectors for which the component $k_{ig\perp}$ in vacuum is real. Each term of this sum is the spin dependent relative intensity of a diffracted beam labelled by $\vec{g}$.

5.2. Spin dependent incoherent back-scattered intensity

The calculation of incoherent intensity follows the same scheme as in the case of general DLEED theory [4] and leads, by using (5.3) and (4.10), to the expression of the spin dependent relative intensity per unit of solid angle in the direction of the detector in the form

$$I_{incoh}^{\uparrow\downarrow} = (\vec{k}_f^- \leftarrow \vec{k}_i^+) = \lim_{s\to\infty}\left(\frac{4\pi^2}{s}\right) k_i \langle|\delta\mathbf{A}^{\uparrow\downarrow}(\vec{k}_{fg}^- \leftarrow \vec{k}_i^+)|^2\rangle \frac{k_{fg\perp}^2}{k_{i\perp}}. \tag{5.5}$$

To obtain the expression useful for numerical calculation quantity $\delta A^{\uparrow\downarrow}$ should be replaced by its relation (4.10), namely

$$I_{incoh}^{\uparrow\downarrow} = (\vec{k}_f^- \leftarrow \vec{k}_i^+) = \frac{4\pi^4 k_i}{AK_{i\perp}} \sum_{p=1}^{p_{\max}} \sum_{p'=1}^{p'_{\max}} \Gamma(p, p', \vec{k}_f^- \leftarrow \vec{k}_i^+) \bar{K}_1^{\uparrow\downarrow}(p, \vec{k}_f^- \leftarrow \vec{k}_i^+) \times K_1^{\uparrow\downarrow}(p', \vec{k}_f^- \leftarrow \vec{k}_i^+) \tag{5.6}$$

where

$$\Gamma(p, p', \vec{k}_f^- \leftarrow \vec{k}_i^+) = \sum_{i=1}^{N} [\langle\sigma_1(p)\sigma_i(p')\rangle - \langle\sigma_1(p)\rangle\langle\sigma_i(p')\rangle] \exp[-\mathrm{i}(\vec{k}_f^- - \vec{k}_i^+)(\vec{T}_i - \vec{T}_i)] \tag{5.7}$$

and A is the area of the unit cell of the substrate surface lattice and N is the number of all chemisorption sites. The expression (5.7), similar to the general DLEED problem, is the Fourier transform on the lattice of the site occupancy pair correlation functions for the pair of sites 1 and i in occupancies p and p', respectively. The relation (5.6) is equivalent to the relation (1.1). In order to underline clearly the differences arising from the introduction of the spin–orbit coupling to the present considerations all stages of the spin dependent DLEED intensity calculations should be now pointed out and analysed. First, the knowledge of the relativistic transition matrices in angular momentum representation for the reference site in any state of occupancy is required. The elements of these matrices are $(1/2)(\exp(2\mathrm{i}\delta_i^\kappa(p)) - 1)$ where the quantity $\delta_i^\kappa(p)$ represents the relativistic scattering phase shift of site i in a occupancy state p ($\kappa = -l - 1$ for $j = l + \frac{1}{2}$ and $\kappa = l$ for $j = l - \frac{1}{2}$). The next step is connected with the calculations of the relativistic effective transition matrix of the p adscatterer located at the reference site in the presence of the other adscatterers (without substrate). The elements of this matrix denoted by $I_1(p, \kappa\mu, \kappa'\mu')$ are given by the relation (3.28) and are expressed by means of the relativistic transition matrices, Clebsh–Gordan coefficients defined in subsection 3.3 and the Green functions due to Pendry's notation [25]. Then, expression (3.27) gives $I_1(p, \vec{k}_f^- \leftarrow \vec{k}_i^+)$, i.e. the relativistic effective transition matrix in the momentum representation. Using now the expression (4.11) the matrix regarded as the relativistic effective transition matrix of the p adscatterer located at the reference site in the presence of the other adscatterers and of the substrate can be determined. Of course, its calculations require the knowledge of matrices $F_1^{\uparrow\downarrow}$ and $F_2^{\uparrow\downarrow}$ whose determination is related to classical SPLEED techniques [21]. Thus, according to the equations (5.6) and (5.7) it remains to perform the Fourier transforms on the reciprocal lattice of the site-occupancy pair correlation functions $\Gamma(p, p')$, which are the structure factors of the adlayer and remain the same as in the case of general DLEED. Different techniques for determining

the correlation functions were discussed [5, 6] as well as tested using the experimental results for the CO/Pt(111) system at the occasion of DLEED calculations [27, 28]. The calculation of $I^{\uparrow\downarrow}_{incoh}$ follows immediately from (5.6) and the spin–orbit induced 'up/down' asymmetry A_{so} given by (2.3) for the spin dependent DLEED (or diffuse SPLEED) intensity can be determined.

The evaluation of the incoherent part of the spin dependent DLEED intensity is a new result which extends the use of the DLEED theory giving the possibility to analyse a much wider experimental data set (one can use both polarized and unpolarized electrons) as well as to correct the theoretical DLEED intensity by the relativistic effects present in the experiment but not taken into account up to now in the theoretical calculations.

Equation (5.6) allows us to discuss the incoherent (diffuse) scattering of the low-energy electrons with a given spin polarization (DSPLEED) at a single-crystal (non-magnetic) surface partially covered with a disordered overlayer. It can be easily seen that the omission of the spin effects in equation (5.6) will lead directly to the equation (1.1) and one is back in the general DLEED theory [4].

6. Application

Let us consider the system CO/Pt(111) for which a mixture of a top and bridge sites occurs. Furthermore, this system has been investigated by many different techniques: HREELS [29], IRAS [30], LEED [31] and DLEED [32]. On the basis of these experimental results the site-occupancy pair correlation functions of CO adsorbed on Pt(111) were determined [27] by a Monte Carlo simulation. The correlation functions will be now used to calculate the spin dependent diffuse LEED intensities. For all calculations the geometrical parameters commonly found in the literature [31] are used and it is assumed that (1) platinum atoms which surround occupied and unoccupied sites have the same location (absence of induced relaxation); (2) C–O and C–Pt bonds remain perpendicular to the surface; (3) C–O bond length is taken to be equal to 1.15 Å; (4) C–Pt distance is taken to be equal to 1.55 Å for a bridge chemisorption site and 1.85 Å for a top site.

Calculation of spin dependent diffuse LEED intensities requires the use of the following computer programs:

- the first one determine the relativistic phase shifts for three elements composing the considered system (A Barbieri, M A Van Hove phase shift package);
- the second one allows calculation of the elements of the carbon monoxide transition matrix in the basis of free spherical waves (equation (3.28) modified to the case of adsorbate being composed of two atoms [33]);
- the third one provides the spin dependent scattering amplitudes of the Pt(111) single-crystal surface (standard SPLEED technique);
- the renormalized spin dependent transition matrix of the molecule in the presence of the substrate is calculated from the fourth one (equation (4.11)) in which the input data are the output data of two previous programs;
- the site-occupancy pair correlation functions and the structure factors (equation (5.7)) are calculated in the fifth program;
- the last program provides the spin dependent diffuse LEED (DSPLEED) intensities (equation (5.6)) and the incoherent scattering asymmetry (equation (2.3)).

To exemplify the presented theory we restrict the calculation to one half order position i.e. (1/2, 1/2). All calculations are performed for normal incidence.

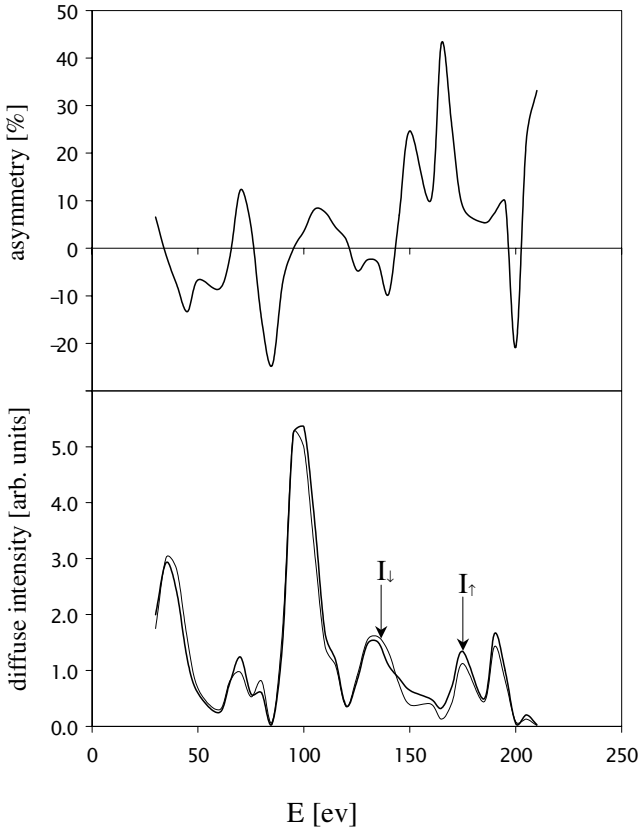

Figure 1. Incoherent scattering asymmetry parameter (top graph) and spin dependent DI-V spectra (bottom graph—bold line for up polarization of the incident electrons, thin line for down polarization) for normal incidence from the CO/Pt(111) system at a CO coverage of 10% for the (1/2, 1/2) position of the backscattered beam.

Figure 1 displays the results of the DSPLEED intensity calculations for the CO coverage of 10% for two different polarizations of the incident electrons (bottom graph) and the resulting incoherent scattering asymmetry (top graph). The spin dependent effects are quite sizeable and have the same order of magnitude as in the case of conventional SPLEED [21]. As predicted the largest values of asymmetry tend to occur near relative minima in the intensities although this correlation is not so strong as it is in scattering from atoms [21] because of multiple-scattering processes taken into account in the present calculations.

Figure 2 shows theoretical predictions for both the DSPLEED intensity and the incoherent scattering asymmetry for an assumed 5% contraction of the spacing between the CO adlayer (10% coverage) and the first Pt layer. One sees clearly that the intensity curves are rather similar. They mainly differ by the height while the structure of spectra is in general reproduced and only small peak shifts can be observed. In contrast the asymmetry curves change dramatically. Thus, the measurement of the incoherent scattering asymmetry is a sensitive method for determining the spacings in the surface region.

Figure 3 presents the results of the DSPLEED intensity and incoherent scattering asymmetry calculation for the CO coverage of 25%. The calculations were performed for two ratios of the number of molecules adsorbed at top sites to the number of molecules adsorbed

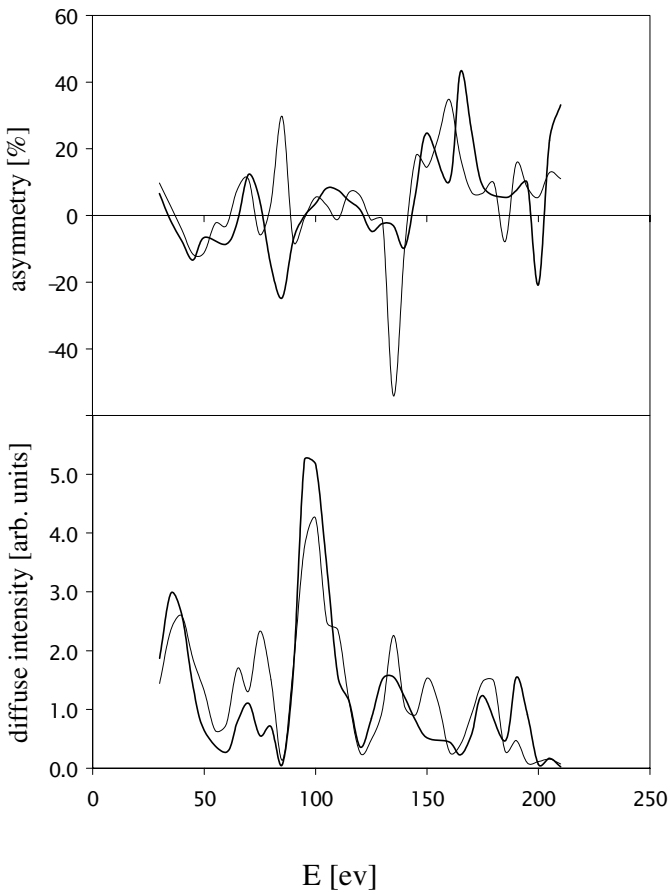

Figure 2. Incoherent scattering asymmetry parameter (top graph) and DI-V spectra (bottom graph) for normal incidence from the CO/Pt(111) system at a CO coverage of 10% for the (1/2, 1/2) position of the backscattered beam; assumed contraction of the adlayer—Pt surface spacing: 0% (bold line) and 5% (thin line).

at bridge sites, this means for two different CO molecule distributions in the adlayer. The changes in distribution can be caused for example by the lattice vibration effects. The curves in figure 3 corresponds to the cases when: (1) the ratio is equal to 18.8 which means that almost all molecules are adsorbed at top sites and (2) the ratio is equal to 0.9 which means that there are now more molecules adsorbed at bridge sites than at top sites. The intensity curves (bottom graph) differ by their height and small peak shifts but they are very similar in their shapes. The incoherent scattering asymmetry (top graph) behaviour changes in a more evident way displaying not only the difference in height and peak positions but also shape modification by appearance of new features.

The example shows how the spin dependence of incoherent scattering can be used for studying the structure of a disordered adlayer. DSPLEED is sensitive to the geometrical parameters characterizing the substrate/disorder adsorbate system as well as to the parameters related to the statistical distribution of the occupied chemisorption sites. In this way, the presented method is complementary to DLEED and can be very helpful for disordered surface structure analysis.

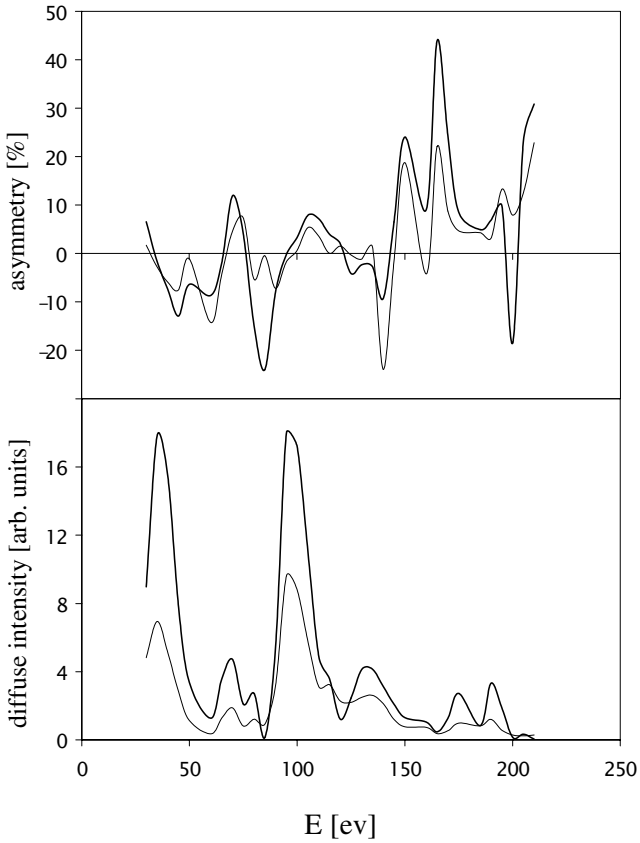

Figure 3. Incoherent scattering asymmetry parameter (top graph) and DI-V spectra (bottom graph) for normal incidence from the CO/Pt(111) system at a CO coverage of 25% for the (1/2, 1/2) position of the backscattered beam; assumed changes in CO molecule distribution: 94.9% at top sites (5.12% at bridge sites) (bold line) and 47.7% at top sites (52.3% at bridge sites) (thin line).

7. Final remarks

In this paper, a theory describing the spin dependent low-energy back-scattering of electrons at a single-crystal surface partially covered with a disordered overlayer of elements has been reported. It must be emphasized that the theoretical treatment of this problem uses both theory and practice of general DLEED theory as well as of classical SPLEED theory. The formalism presented in this paper is original in context of the usual DLEED and SPLEED formalisms.

Let us note that the DLEED intensities present a background which is very weak compared with the diffracted intensities. This is due to three causes (1) in most LEED experiments adelements have a smaller Z than substrate atoms and consequently, adelements have a smaller scattering amplitude than substrate atoms; (2) the adlayer is a less closely packed arrangement of elements than the substrate and consequently, the total incoherent intensity, coming from the scattering at the adelements, is smaller than the sum of the diffracted intensities; (3) in contrast to diffracted intensities, which are concentrated in a small number of directions, the total incoherent intensity is distributed into a solid angle of 2π and, consequently, the relative incoherent intensity per unit of solid angle is weaker than a diffracted beam intensity. Thus, the DLEED intensity measurements and their analysis are a very difficult task. However, it was

shown that this method is sensitive to the geometrical parameters as well as to the short-range order and can be successfully used for the determination of the local geometry in the disordered adlayer [34]. It can be expected that the present considerations bring some new possibilities for the disordered surface structure analysis. The use of polarized beam enlarges the data base giving the evident sensitivity of incoherent scattering asymmetry to the geometrical parameters (figure 2) and to the statistical distribution of adelements (figure 3).

Concerning the theoretical part of this work, some continuations are envisaged. The theory can be expanded to the case of disordered magnetic surfaces. Polarization effects due to the exchange interaction can be introduced by solving the Dirac equation with an effective potential including the magnetic interaction contribution. Magnetic DSPLEED will give the possibility of information about the layer, temperature and field dependent magnetization of disordered surfaces, especially in the region of phase transitions, in the case of diluted magnetic surfaces or the magnetic surface amorphization.

It is evident that the neutron scattering by magnetic samples shows the appearance of magnetic fluctuations in the vicinity of the Curie temperature [35]. The fluctuations are then a very convenient background for modelling randomly distributed elements represented by the magnetic moments. Thus, we can expect the confirmation of this background by means of the electron scattering when the polarization of the electron beam is taken into account. From the theoretical point of view the present theory is a relativistic extension of the theory of neutron scattering in the case of its diffuse nature [36] and it can be easily applied to the magnetic surface fluctuation investigations.

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