

DIFFUSE LEED INTENSITIES OF DISORDERED CRYSTAL SURFACES

II. Multiple scattering on disordered overlayers

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The diffraction of low energy electrons from disordered overlayers adsorbed on ordered substrates is treated theoretically by an extension of Beeby's multiple scattering method. A lattice gas model is assumed for the disordered adsorbate layer. Multiple scattering within a certain area around each atom – each atom of the overlayer and within the ordered substrate – is treated self-consistently, the remaining contributions to the total scattering amplitude being averaged. The theory can be used in the limiting cases of random distribution and of long range order within the adsorbate layer.

1. Introduction

By analyzing the diffuse diffraction patterns of disordered surfaces one can get information about the adsorbate–adsorbate and adsorbate–substrate interactions, such as the binding energies, the activation energies for diffusion and the interaction force laws [1–6]. There have been several qualitative investigations to extract some information on the interaction energies between ad-atoms by analyzing the half-widths of the angular profile of diffuse LEED beams as a function of temperature and coverage [6–13,29].

It is usually assumed that the influence of multiple scattering effects on the angular profile is weak and one can use the kinematic theory to interpret the experimental results, especially in cases where only the temperature dependence of the half-widths of the angular profile is measured with constant energy of the incident beam. As long as this assumption is valid the angular profile is given by the Fourier transform of the averaged correlation functions superimposed by the scattering factors of the structural elements. Nevertheless, a dynamical calculation is necessary to show the limits of a kinematic treatment.

Until now, the only dynamical scattering theory for disordered adsorbed overlayers has been published by Duke and Liebsch [14]. They used a nearest neighbour Ising model to describe the statistical distribution of adsorbed atoms and

evaluated the multiple scattering amplitudes in the quasi-crystalline analysis. This theory describes the multiple scattering processes in a perturbation series expansion using pair correlation functions to evaluate consecutive scattering events appearing in the perturbation series. The average over all possible scattering paths is taken and finally the perturbation series is summed up again. In that way the effective scattering amplitude of each atom becomes independent from its actual surrounding (not independent from the statistical distribution and temperature) which leads to a lack of self-consistency. The applicability of this theory is therefore limited.

To overcome that difficulty, and also to include a longer range of interaction forces, we introduce here a multiple scattering scheme which explicitly considers the occupation of adsorption sites within a certain neighbourhood around each adsorbed atom. That means it is necessary to calculate a different scattering amplitude for each atom with a different neighbourhood, defining the scattering amplitude of an atom by summing up all scattering events which end in this atom. This method is formally equivalent to that used in multiple scattering theories for ordered structures where one plane has to be divided into subplanes in case of non-primitive unit cells [15–17].

To make the number of matrices which have to be calculated still tractable, the neighborhood of an atom is restricted to the nearest or next nearest neighbors. By this method the multiple scattering events up to all orders are included within a certain area around each atom. In this paper this area will be referred to as the “area of multiple scattering” AMS (see Part I). Scattering events with a larger distance between two adsorbate atoms are averaged. This procedure is justified by the result that the major contributions to the total scattering amplitude arise from single scattering and multiple scattering between nearest neighbors. Furthermore, only the disordered adsorbate layer is involved in averaged scattering amplitudes, while multiple scattering within the ordered substrate is treated selfconsistently.

The theory developed here uses correlation functions defined for configurations of atoms, a method which has two advantages. First, the nearest neighbor (NN) and the next nearest neighbor (NNN) interactions and even interactions between atoms further apart (usually ignored in statistical models) can be included in the multiple scattering formalism as the same type of correlation functions is used in the description of the statistical distribution of adsorbed atoms and in the description of multiple scattering amplitudes. Second, the connection between the interactions of the adsorbed atoms and the resulting diffraction picture can be seen more clearly. Once the scattering amplitudes for each configuration have been calculated, the further treatment is exactly the same as in the kinematic theory which is well developed for the interpretation of diffuse X-ray diffraction patterns (see also part I).

The treatment of the multiple scattering problem given here uses the formalism developed by Beeby [15]. The dimension of the matrix to be inverted is greatly increased by the extension to disordered overlayers, but an approximate solution is possible for a simplified model, and a calculation may be useful in studying the

extent to which dynamical effects limit the validity of a kinematical interpretation of the measured angular beam profiles [30].

2. Model of the disordered surface

A monolayer containing the atoms A and B is adsorbed on a perfectly ordered substrate of atoms C. The atoms A and B are statistically distributed in the adsorbed layer and can only occupy lattice points as adsorption sites (fig. 1).

This model also describes the special cases of incomplete adsorbed layers, steps, and terraces, and even one-dimensionally disordered overlayers. The atoms B may be replaced by a vacancy. The model is easily extended to the case of different distances of the two atoms A and B to the underlying layer, which is not assumed here for the sake of convenience.

As a result of multiple scattering the scattering amplitude of each atom, described by the T -matrix in Beeby's formalism, depends on its neighborhood. Including only the nearest neighbors there are for example in the (100) face of a fcc crystal five possible adsorption sites which can be occupied by two sorts of atoms. That makes $2^5 = 32$ different configurations. With r neighbors there are generally $N = 2^{r+1}$ different configurations, half of them with central atom A, or B respectively.

Fig. 2 shows how the configurations are linked together and also that only certain configurations can follow one another (in this example only 8 of 32 possible ones).

The only statistical parameters entering the multiple scattering theory (and these are also the only statistical parameters which can be determined by analyzing the diffraction picture) are the correlation functions of these configurations. The connection between these parameters and the binding energies and thermodynamical quantities such as the heat of adsorption, etc., is not discussed here (see part I). It is assumed that a numerical or analytical solution of the statistical problem of finding the equilibrium distribution at given interaction energies is possible, see for example a recent article by Doyen et al. [24].

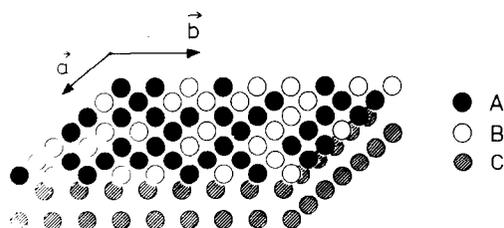


Fig. 1. Model of the surface.

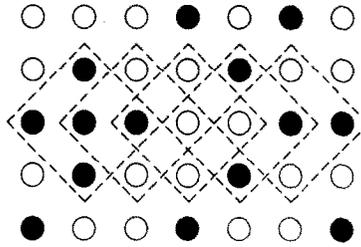


Fig. 2. Linking and overlapping of the configurations.

Let $e_{mn}(\mathbf{P}, \mathbf{P}')$ be the operator which sets the central atom of a configuration of type m on the lattice point \mathbf{P} and the central atom of type n on the lattice point \mathbf{P}' ($m, n = 1, \dots, N$). The central atom of a configuration of type m is further denoted as an atom of "type" m for the sake of convenience.

The probability to find two atoms of type m and n at the distance $\mathbf{P} - \mathbf{P}'$ is given by

$$p_{mn}(\mathbf{P} - \mathbf{P}') = \langle e_{mn}(\mathbf{P}, \mathbf{P}') \rangle,$$

and is a function of direction and distance only because of the homogeneity of the surface.

The a-priori probabilities p_m and the coverage θ_A, θ_B of the surface with the atoms A and B are given by the relations

$$p_n = \lim_{\mathbf{P} - \mathbf{P}' \rightarrow \infty} p_{mn}(\mathbf{P} - \mathbf{P}')$$

$$\theta_A = \sum_m^{1, N/2} p_m, \quad \theta_B = \sum_m^{N/2+1, N} p_m,$$

They cannot be chosen independently from the correlation functions $p_{mn}(\mathbf{P} - \mathbf{P}')$.

It should be pointed out that the probabilities and correlation functions, as used here, are related to configurations of atoms and are not necessarily the same which are used in the statistical analysis of the equilibrium distribution, and which are either related to single atoms (smallest possible configuration where the correlation function is denoted as the site occupancy pair-correlation function, or to configurations of atoms used in statistical methods, including more than nearest neighbor interactions [27,28]. The size of these configurations and their number depend on the range of the interaction forces between adsorbed atoms, called the "area of (direct) thermodynamic interaction ATI" (see Part I). This area of interaction may be smaller or larger than the area of multiple scattering (usually smaller) and the related probabilities are defined for two different sets of configurations.

If the area of direct interaction is smaller than the area of multiple scattering, a new set of sequence probabilities is needed and some of the configurations get

equal sequence probabilities; if the area of direct interaction is larger, a sub-set of configurations is described by the same scattering amplitude (the simplest example for that case is given by the kinematical treatment).

The equivalents of the description of the surface with a set of configurations and their related probabilities and the description with pair correlation functions is easily seen in $D-1$. If only nearest neighbor interactions are assumed the pair correlation functions are given by two parameters: $p_{AA} = \alpha_1, p_{AB} = 1 - \alpha_1, p_{BA} = \alpha_2, p_{BB} = 1 - \alpha_2$. The correlation functions for each distance ja are given by the elements of the matrix

$$(p(1))^j = \begin{pmatrix} \alpha_1 & 1 - \alpha_1 \\ 1 - \alpha_2 & \alpha_2 \end{pmatrix}^j.$$

For the multiple scattering formalism configurations of the type

AAA, AAB, ABA, ABB, ... ,

are used and their correlations are simply given by

$$p_{AAA} = \alpha_1, \quad p_{AAB} = 1 - \alpha_1, \quad p_{ABA} = 1 - \alpha_2, \quad p_{BBA} = 1 - \alpha_2, \quad \dots,$$

resulting in an (8×8) matrix, still having the same eigenvalues as the (2×2) matrix described above.

In any case, the correlation functions and probabilities which are determined by the interaction energies – even if only a numerical solution is given – are easily transformed into the form related to configurations used in the multiple scattering formalism.

So far, only configurations within the adsorbed layer have been considered. Through multiple scattering as many different scattering amplitudes are induced in the second and further layers as in the adsorbed layer. Thus, statistics of the adsorbed layer are continued into the substrate.

3. Calculation of scattering amplitudes

In Beeby's multiple scattering approach [15] the crystal is divided into layers in which all atoms have equivalent sites. For non-primitive plane unit cells the layers have to be divided into subplanes. The details of the theory are given explicitly in [25]. Here only those relations shall be repeated which are relevant in further calculations.

The intensity scattered into k' is given by

$$I(k, k') = R \left| \frac{-8\pi^2 i}{Ak'_\perp} \sum_\nu \sum_{L, L'} Y_L(\Omega_{k'}) T_{LL'}^\nu(k) Y_{L'}^*(\Omega_k) \exp[i(k - k') \cdot d_\nu] \right|^2 \times \sum_g \delta(k_\parallel - k'_\parallel + g). \tag{1}$$

\mathbf{k} , \mathbf{k}' are the wave vectors of the incoming and outgoing wave; $|\mathbf{k}| = (E - V_0)^{1/2}$, and V_0 has an imaginary part to account for the strong inelastic damping of the wave inside the crystal. A is the area of the unit cell and

$$R = |k'_{\perp \text{ext}}| / |k_{\perp \text{ext}}|$$

is the Lorentz factor. The quantities $T_{LL'}^{\nu}(\mathbf{k})$ are matrices in the partial wave representation and represent all scattering processes which end in an atom in plane ν . They are given by the following system of linear equations

$$T_{LL'}^{\nu}(\mathbf{k}) = t_{LL'}^{\nu}(\mathbf{k}) + \sum_{L_1, L_2} t_{LL_1}^{\nu}(\mathbf{k}) \sum_{\mu} G_{L_1 L_2}(\mathbf{k}) T_{L_2 L'}(\mathbf{k}). \quad (2)$$

The electron propagators $G_{L_1 L_2}(\mathbf{k})$ can generally be evaluated by

$$\begin{aligned} G_{L_1 L_2}^{\nu \mu}(\mathbf{k}) &= \sum_{\mathbf{P}} G_{L_1 L_2}(\mathbf{P} + \mathbf{d}_{\mu} - \mathbf{d}_{\nu}) \exp[-i\mathbf{k} \cdot (\mathbf{P} + \mathbf{d}_{\mu} - \mathbf{d}_{\nu})] \\ &= \sum_{\mathbf{P}} \sum_{L_3} 4\pi k C(L_1, L_2, L_3) i^{l_1} h_{l_3}^{(1)}(|\mathbf{k}_0| |\mathbf{P} + \mathbf{d}_{\mu} - \mathbf{d}_{\nu}|) \\ &\quad \times Y_{L_3}(\Omega_{\mathbf{P} + \mathbf{d}_{\mu} - \mathbf{d}_{\nu}}) \exp[-i\mathbf{k} \cdot (\mathbf{P} + \mathbf{d}_{\mu} - \mathbf{d}_{\nu})]. \end{aligned} \quad (3)$$

The summation in eq. (3) should skip the point

$$\mathbf{P} \neq \mathbf{0} \quad \text{if} \quad d_{\mu \perp} - d_{\nu \perp} = 0.$$

$h_l^{(1)}$ and $Y_L(\Omega) = Y_{l,m}(\Omega)$ are the spherical Hankel functions of the first kind and the spherical harmonics, and

$$C(L_1, L_2, L_3) = \int Y_{l_1, -m_1}(\Omega) Y_{l_2, m_2}(\Omega) Y_{l_3, m_3}(\Omega) d\Omega, \quad L = (l, m).$$

As Tong and Rhodin [19] have shown, eq. (3) can be summed up more easily in reciprocal space when $d_{\mu \perp} - d_{\nu \perp} \neq 0$.

The quantities

$$t_{L_1, L_2}^{\nu}(\mathbf{k}) = k^{-1} \exp(i\eta_l) \sin \eta_l \delta_{L_1 L_2}$$

are diagonal matrices describing a single scattering event, η_l are the phase shifts.

Eq. (1) can be written as

$$I(\mathbf{k}, \mathbf{k}') = R |F(\mathbf{k}, \mathbf{k}')|^2 \sum_{\mathbf{g}} \delta(\mathbf{k}_{\parallel} - \mathbf{k}'_{\parallel} + \mathbf{g}), \quad (4)$$

where $|F(\mathbf{k}, \mathbf{k}')|^2$ is taken as a generalized structure factor of a unit cell which is extended over all layers of the crystal (this expression has been used in Part I).

There are no equivalent sites in a disordered overlayer and in the set of eqs. (2) one would have to take $T^{\nu, P}(\mathbf{k})$ instead of $T^{\nu}(\mathbf{k})$. An exact solution is no longer possible. If one uses a perturbation series expansion or a self-consistent method, the scattering amplitude has to be averaged in any case. In this method of averaging the

amplitude the fact is neglected that in the experiment the averaged intensities are observed. That means, the area of the multiple scattering has to be extended such that the averaged contributions could have been neglected anyway. On the other hand, these contributions contain all the multiple scattering inside the ordered substrate which cannot be omitted and remains unaltered by the averaging process.

In fig. 3 the calculated intensities of two different beams of the Ag(111) face are shown, for which the intra-layer scattering is included only up to nearest or next-nearest neighbors. The multiple scattering between the layers (inter-layer scattering) is calculated with the RFS scheme of Pendry [18]. The agreement between these curves and the exact calculation is rather good for the lower energies, indicating that the major part of the scattering amplitude arises from multiple scattering between nearest neighbors. For a disordered overlayer, including the exact calculation of the multiple scattering in the ordered substrate, the agreement should be much better.

Let us consider multiple scattering within the disordered overlayer alone. It has already been pointed out that to each atom with a different neighborhood corresponds a different scattering amplitude represented by a τ matrix in the angular momentum representation following the notation of Beeby.

Including n neighbors, which lie within a radius $|P| \leq r$, one gets $N = 2^{n+1}$ different τ matrices. As in the case of ordered layers the calculation of the τ matrices is best done by summing up all scattering events which end in a single atom. This is the central atom of the configurations defined in section 2.

The scattering matrix for the central atom of the configuration of type m at

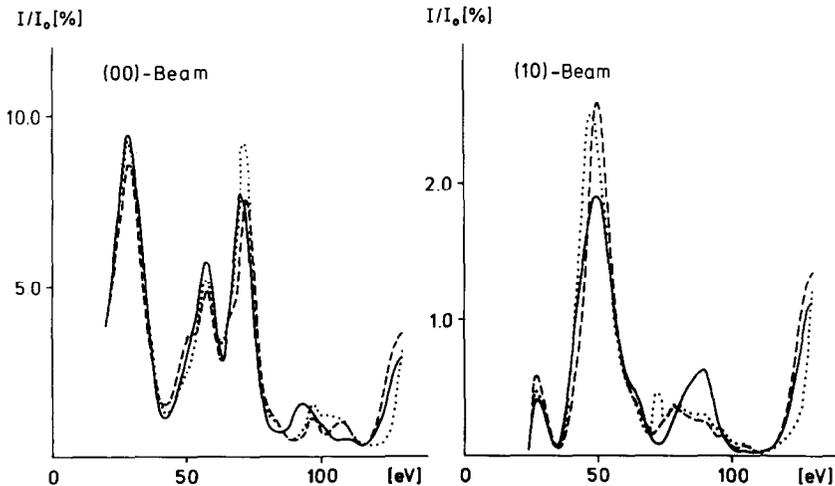


Fig. 3. Calculated I-V spectra for Ag(111) for normal incidence and zero temperature. Broken line: nearest neighbors; dotted line: next nearest neighbors are included for intra-layer scattering. Solid line: exact calculation (~ 500 lattice points). Five phase shifts are used.

point P_0 is in that way given as

$$\begin{aligned} \tau_m(\mathbf{k}) = & t_m(k) + t_m(k) \sum_{|\mathbf{P}-\mathbf{P}_0| \neq 0} \sum_n^{1,N} G(\mathbf{P}-\mathbf{P}_0) \exp[-i(\mathbf{k} \cdot (\mathbf{P}-\mathbf{P}_0))] \\ & \times e_{mn}(\mathbf{P}, \mathbf{P}_0) \tau_n(\mathbf{k}) \\ & + t_m(k) \sum_{|\mathbf{P}-\mathbf{P}_0| > r} G(\mathbf{P}-\mathbf{P}_0) \exp[-i\mathbf{k} \cdot (\mathbf{P}-\mathbf{P}_0)] \overline{\tau_n(\mathbf{k})}, \end{aligned} \quad (5)$$

where

$$t_m(k) = \begin{cases} t_A = k^{-1} \exp(i\eta_{l,A}) \sin \eta_{l,A}, & m = 1, \dots, \frac{1}{2}N; \\ t_B = k^{-1} \exp(i\eta_{l,B}) \sin \eta_{l,B}, & m = \frac{1}{2}N + 1, \dots, N. \end{cases}$$

The average of the site occupancy operators in the second term of the right hand side of eq. (5) is necessary because the configuration m can be followed by several other configurations all with the same central atom.

That means that the average is taken only over scattering processes which start at a point P with $|\mathbf{P}-\mathbf{P}_0| > r$ and end at point P_0 after intermediate scattering with the radius r , and also of similar processes of higher order.

It should be pointed out that multiple scattering processes with maximum distance r between two scattering events are treated self-consistently, while for a greater distance an average is taken. If one had to calculate scattering from a single layer only, the use of an averaged amplitude would be senseless. However, when treating all layers in the same manner the formal addition of this term is necessary in order to take into account the periodicity of the substrate.

In the case $r = 0$ only two different scattering amplitudes remain, the correlation function is constant for all distance, and the probabilities to find an atom A or B are θ_A and θ_B respectively, hence

$$\tau_A(\mathbf{k}) = t_A(k) + t_A(k) \sum_P G(\mathbf{P}-\mathbf{P}_0) \exp[-i\mathbf{k} \cdot (\mathbf{P}-\mathbf{P}_0)] \{\theta_A \tau_A + \theta_B \tau_B\}. \quad (6)$$

In that case all adsorbed atoms of the same kind are represented by a single τ matrix which becomes independent of the temperature. Eq. (5) may be written as

$$\tau_m(\mathbf{k}) = t_m(k) + t_m(k) \sum_n^{1,N} G_{mn}^{\nu\nu}(\mathbf{k}) \tau_n(\mathbf{k}). \quad (7)$$

The layers of the substrate have to be divided into the same configurations as the disordered overlayer, and for all layers the same statistics are valid. The scattering matrices for the whole adsorbate-substrate system are therefore easily obtained:

$$T^{m,\nu}(\mathbf{k}) = t_{m,\nu}(k) + t_{m,\nu}(k) \sum_\mu \sum_n G_{mn}^{\mu\nu}(\mathbf{k}) T^{n,\mu}(\mathbf{k}), \quad (8)$$

$$t_{m,\nu}(k) = t_c \equiv k^{-1} \exp(i\eta_{l,c}) \sin \eta_{l,c}, \quad \text{for } \nu \geq 2,$$

with propagator matrices:

$$G_{mn}^{\mu\nu}(\mathbf{k}) = \sum_P^{|\mathbf{P}| \leq r} G(\mathbf{P} + \mathbf{d}_\mu - \mathbf{d}_\nu) \exp[-i\mathbf{k} \cdot (\mathbf{P} + \mathbf{d}_\mu - \mathbf{d}_\nu)] p_{mn}(\mathbf{P}) + \sum_P^{|\mathbf{P}| > r} G(\mathbf{P} + \mathbf{d}_\mu - \mathbf{d}_\nu) \exp[-i\mathbf{k} \cdot (\mathbf{P} + \mathbf{d}_\mu - \mathbf{d}_\nu)] P_n, \quad (9)$$

$|\mathbf{P}| \neq 0$ for $\mathbf{d}_\mu - \mathbf{d}_\nu = 0$.

In this way all those scattering processes are correctly calculated to which the adsorbate does not contribute. This may best be seen by setting in eq. (8) all $t_{m,\nu}(\mathbf{k}) = t(\mathbf{k})$. The system of equations is then reduced to that of the ordered crystal.

Eq. (2), which solves the problem of multiple scattering in ordered crystals exactly, is extended by eq. (8) for a disordered overlayer. The multiple scattering within a certain neighborhood is calculated exactly, and the necessary average is restricted to the less important atoms further apart. From fig. 3 it appears that in many cases configurations with nearest neighbors may be sufficient. The scattering matrices $T^{m,\nu}(\mathbf{k})$ may then be replaced by the average for $\nu \geq 3$.

In fig. 4 an example is given to clarify the averaging of scattering processes. The electron may first be scattered by an atom A or B; these two possibilities are taken with their corresponding probabilities in the cases 2 and 3, but not in case 1, where the site of the first scattering event is included in the area of multiple scattering.

The T matrices depend on the direction of the wave vector of the incoming wave. As in disordered systems generally $k_{\parallel} \neq k_{\parallel} + \mathbf{g}$, where \mathbf{g} is a reciprocal lattice vector it is necessary to show that the equation for the scattered intensity is consis-

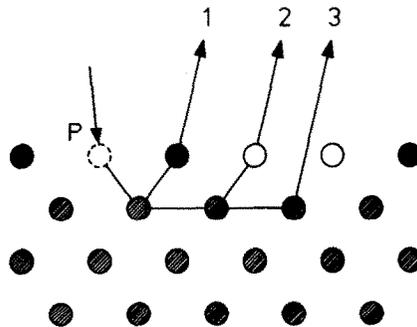


Fig. 4. The first scattering event at point P is included in the area of multiple scattering in case 1, the average is taken in cases 2 and 3. Intermediate scattering within the ordered substrate is not changed by averaging.

tent with the requirement of invariance under time reversal. The T matrices themselves may vary under time reversal but the scattered intensity is not changed as shown in appendix B.

The number of different scattering matrices to be computed can be reduced drastically by considering symmetry relations. This is usually possible for normal incidence or if the incident beam lies within a mirror plane.

The intensity scattered into the direction k' is given by

$$\overline{I(k, k')} = R \left\langle \sum_{P, P'} \sum_{m, n} e_{mn}(P, P') F_m(k, k') F_n^*(k, k') \exp[i(k - k') \cdot (P - P')] \right\rangle, \quad (10)$$

$$F_m(k, k') = \frac{-8\pi^2 i}{A k_{\perp}'} \sum_{\nu} \sum_{L, L'} Y_{L\nu}(\Omega_k) T_{LL}^{m\nu}(k) Y_{L\nu}^*(\Omega_{k'}) \exp[i(k - k') \cdot d_{\nu}], \quad (11)$$

$$P = m_1 a + m_2 b, \quad P - P' = j_1 a + j_2 b.$$

$F_m(k, k')$ represents the generalized structure amplitude containing all scattering processes which end in an atom of type m and the summation over layers is already performed.

As Wilson [26] and others have shown, one obtains after performing the average and replacing the site occupancy operators by their corresponding probabilities

$$\overline{I(k, k')} = R \sum_{j_1} \sum_{j_2} (N_1 - |j_1|) (N_2 - |j_2|) \overline{FF_{j_1 j_2}^*(k, k')} \exp[-i(k - k') \cdot (j_1 a + j_2 b)], \quad (12)$$

with the mean value of the generalized structure factors:

$$\overline{FF_{j_1 j_2}^*(k, k')} = \sum_m \sum_n p_m p_{mn}(j_1, j_2) F_m F_n^*(k - k');$$

$F_m F_n^*$ has to be taken for $(-j_1, -j_2)$, N_i = number of unit cells in both directions.

To compute the mean value it is necessary to know the correlation functions for all distances. The sum in (12) may be evaluated numerically, however, much computer time is needed. An approximate solution is possible in most cases by assuming the correlation functions for the two lattice directions to be independent, thus reducing the problem to that of one-dimensional disorder for which an analytical solution exists [27]. A detailed review of this procedure is given in Part I.

In Part IV of this work an example is given of the way in which the measured beam profile can be analyzed in a pseudokinematic way, when the dependence on k and k' of the mean value $\overline{FF_{j_1 j_2}^*}$ is replaced by a linear dependence on the scattering angle.

4. Discussion

The system of eqs. (8) gives only a formal solution of the multiple scattering problem of a disordered adsorbed overlayer. A practical evaluation is not directly

possible because of the dimension of the matrix to be inverted. Even for an ideal lattice the direct solution is inefficient. Therefore, several methods have been developed for ideal lattices in which the forward scattering for all beams or only the direct beam is calculated exactly, and the back-scattering is treated in a perturbation series [18,20–23]. In all these methods the perturbation expansion is calculated in \mathbf{k} -space. This is generally possible also in the case of a disordered system, but then a back-transformation is necessary, or the calculation has to start again for each direction \mathbf{k}' . The explicit calculation of the scattering matrices $T^{m,\nu}(\mathbf{k})$ has the advantage that they are independent of the direction of \mathbf{k}' and thus it is necessary only once to get all diffuse streaks. A method to solve eq. (8) iteratively for a one-dimensional disordered overlayer is discussed in the appendix A. For two-dimensionally disordered overlayers, or, if more than the nearest neighbors have to be considered, the number of different scattering matrices becomes indeed so large that a calculation in \mathbf{k} -space may be more advantageous.

A dynamical calculation of scattering amplitudes cannot be avoided in determining the structure of ordered overlayers. In several cases a remarkably good agreement between experiment and theory has been obtained, so that it was possible to differentiate between several possible adsorption sites. However, the exact determination of the binding distance remains uncertain. The main difficulty is not due to the calculation of multiple scattering. It is mainly caused by the approximation made in calculating the phase shifts, the potential step between vacuum and crystal, the temperature effects, and the uniform damping inside the crystal. All these effects generally produce only small changes in the energy profile but they limit the accuracy of structure determination essentially. In case of disordered overlayers these difficulties should increase as the calculation of phase shifts is more uncertain, and also the multiple scattering problem is solved only approximately.

The determination of the adsorption sites and atomic distances can best be done on ordered overlayers. In the case of disorder it is more suitable to analyze beam profiles instead of energy profiles and to extract the statistical parameters and binding energies by measuring the temperature dependence of beam profiles. An example of an analysis, in which the explicit calculation of the $F_m(\mathbf{k}, \mathbf{k}')$ is avoided, is given in Part IV. It can be shown that direct evaluation of the measured profile is possible if the generalized structure amplitudes $F_m(\mathbf{k}, \mathbf{k}')$ can be approximated by a linear expansion over the full width of the beam. The angle between two beams is about 10–15°, for electron energies about 100 eV. The scattering amplitude of a free atom shows strong angular structure but no sharp interferences. By multiple scattering in the crystal the generalized structure amplitude becomes explicitly dependent on \mathbf{k} and \mathbf{k}' . As the main contribution arises from multiple scattering between nearest neighbors no sharp interferences are expected. But the generalized scattering amplitudes of eq. (11) also contain the sum of amplitudes of all layers and as a consequence the angular dependence of $F_m(\mathbf{k}, \mathbf{k}')$ can increase in such a way that the beam profiles are strongly deformed. In any case, there should be no additional peaks as only a few layers take part in the scattering.

The influence of multiple scattering is also strongly energy-dependent, so that by measuring beam profiles at different energies it should be possible to extract an energy-independent part which depends on the statistics only.

Appendix A. Calculation of scattering matrices for one-dimensional overlayers.

In several cases the diffraction pattern of adsorbed overlayers shows streaks only in one direction. This means that on the surface ordered chains are adsorbed, showing some disorder with respect to their position and composition. The latter case, applied to the model described in section 2 means that not all possible adsorption sites in the direction a are occupied while periodicity remains in the direction b . There shall be only one kind of adsorbed atom and therefore $t_B(k) \equiv 0$. The configurations are built up by chains of atoms. In the direction a neighboring chains up to the distance ra_0 are included. That corresponds to $N = 2^{2r+1}$ different configurations within one layer.

The system of equations (8) must be reduced to make a practical calculation possible. This is achieved by expressing the correlation function as the sum of its mean value and its deviation from the mean value:

$$p_{mn}(j) = p_m + d_{mn}(j) . \quad (13)$$

Eq. (8) takes the form:

$$\begin{aligned} T^{m,\nu}(k) = & t_{m,\nu}(k) + t_{m,\nu}(k) \sum_{\mu} G^{\nu\mu}(k) \sum_n T^{n,\mu}(k) p_n \\ & + t_{m,\nu}(k) \sum_{\mu} \sum_j^{-r,r} G_s^{\nu\mu}(k, j) \sum_n d_{mn}(j) T^{n,\mu}(k) , \end{aligned} \quad (14)$$

$$t_{m,\nu}(k) = \begin{cases} t_A(k), & \nu = 1, & m = 1, \dots, N/2, \\ 0, & \nu = 1, & m = N/2 + 1, \dots, N, \\ t_c(k), & \nu \geq 2, \end{cases}$$

$$G_s^{\nu\mu}(k, j) = \sum_{j_2} G(ja + j_2b + d_\nu - d_\mu) \exp[-ik \cdot (ja + j_2b + d_\nu - d_\mu)]$$

$$j_2 \neq 0 \quad \text{at} \quad d_\nu - d_\mu = 0 \quad \text{and} \quad j = 0 . \quad (15)$$

The propagator matrices $G^{\nu\mu}(k)$ are defined in eq. (3). The solution of eq. (14) with only the first two parts of the right hand side represents the averaged part alone:

$$\overline{T^{m,\nu}(k)} = t_\nu(k) + t_\nu(k) + \sum_{\mu} G^{\nu\mu}(k) \sum_n p_n \overline{T^{n,\mu}(k)} . \quad (16)$$

All N scattering matrices of one layer become equal in this way and one can write

$$\overline{T^\nu(k)} = t_\nu(k) + t_\nu(k) \sum_\mu G^{\nu\mu}(k) \overline{T^\mu(k)} \sum_n p_n ;$$

$$\text{for } \mu = 1: \sum_n^{1,N} p_n = 1 ; \quad \mu \geq 2: \sum_n^{1,N/2} p_n = \theta , \tag{17}$$

due to the fact that in the adsorbed layer not all adsorption sites are occupied.

Eq. (17) describes the multiple scattering in an ideal crystal with a damped first layer and could have been obtained directly from eq. (2).

With averaged scattering matrices $\overline{T(k)}$ eq. (14) takes the form:

$$T^{m,\nu}(k) = \overline{T^\nu(k)} + \overline{T^\nu(k)} \sum_\mu \sum_j^{-r,r} G_s^{\nu\mu}(k, j) \sum_n d_{mn}(j) T^{n,\mu}(k) ,$$

$$j \neq 0 \quad \text{for} \quad d_\mu - d_\nu = 0 . \tag{18}$$

Eq. (18) is only a rewriting of eq. (8). The matrices $\overline{T^\nu(k)}$ contain all the scattering processes within the ordered substrate correctly, and all scattering processes in which the overlayer participates are averaged. I.e., most of the scattering is already included and an iteration should be convergent. The first step of the iteration is especially easy as only the adsorbed layer has to be considered:

$$T_{(1)}^{m,\nu} = \overline{T^\nu} + \overline{T^\nu} \sum_j^{-r,r} G_s^{\nu,1}(k, j) \overline{T^1} \sum_n^{1,N/2} d_{mn}(j) ;$$

the next steps of the iteration are:

$$T_{(i+1)}^{m,\nu} = \overline{T^\nu} + \overline{T^\nu} \sum_\mu \sum_j^{-r,r} G_s^{\nu\mu}(k, j) \sum_n d_{mn}(j) T_{(i)}^{n,\mu} . \tag{19}$$

The deviation from the mean value is only strong for the first 2 or 3 layers and becomes less important with increasing depth. Therefore, the iteration may be done for two or three layers only, and for the other ones the already calculated average is taken.

The iteration procedure has to be convergent also in the case of long range order. This can be used for testing the convergence as it is possible to compare the results with those of more exact calculations.

In case of convergence an exact solution of eq. (8) is obtained. The only approximation is the averaging of the scattering amplitudes of those processes which have more than a few atomic distances between two scattering events within the disordered overlayer.

The method of first calculating the mean value exactly, and then the differences iteratively, has several other advantages: The averaged scattering matrices once cal-

culated can be stored and a test can be made on the number of configurations and layers that are necessary in eq. (14) to get correct results. Furthermore, several statistical models can be used at constant coverage up to long range order.

One gets all beam profiles of the whole diffraction picture by only one matrix inversion and a relatively time-consuming iteration procedure.

Appendix B. Invariance under time reversal.

The equation for the scattered intensity must be consistent with the reciprocity theorem whether the crystal is ordered or not, and for scattering from molecules as well. This means that the scattered intensity remains unchanged when the wave vector of the incoming wave k is replaced by $-k'$, and k' by $-k$, where generally $k'_{\parallel} \neq k_{\parallel} + g$.

To prove this invariance it is sufficient to look at scattering from the disordered overlayer only; the derivation remains valid for scattering of the ordered substrate as well.

The scattered intensity is in that case given by eq. (10)

$$I(k, k') = R \langle \sum_P \sum_m e_m(P) F_m(k, k') \exp[-i(k - k') \cdot P] \rangle^2, \quad (20)$$

where

$$F_m(k, k') = \frac{-8\pi^2 i}{A k'_{\perp}} \sum_v \sum_{LL'} Y_L(\Omega_{k'}) \tau_{LL'}^m(k) Y_{L'}^*(\Omega_k). \quad (21)$$

To get a better understanding of the influence of k on the scattering matrices it is convenient to use the expansion of a perturbation series obtained by iterating eq. (5)

$$\begin{aligned} \tau_m(k) &= t_m(k) + t_m(k) \sum_{P_1 \neq P_0} \exp[-ik(P_1 - P_0)] \sum_n G_{mn}(P_1 - P_0) t_n(k) + \dots \\ &+ \sum'_{P_j, P_{j-1}, P_0} \exp[-ik \cdot (P_j - P_0)] \sum_{n_1, n_2, n_j} t_m(k) G_{mn_1}(P_1 - P_0) t_{n_1} G_{n_1 n_2}(P_2 - P_1) \\ &\times t_{n_2}(k) \dots G_{n_{j-1} n_j}(P_j - P_{j-1}) t_{n_j}(k). \end{aligned} \quad (22)$$

The prime on the summation symbol indicates that $P_j \neq P_{j-1}$.

The phase factors $\exp[ik \cdot (P_{j-1} - P_j)]$ occurring in the series expansion partly cancel out each other and there remains only the difference of the phases between the first scattering event at point P_j and the last scattering event at point P_0 . The sums over P_j can be rearranged and put together to give

$$\tau_m(k) = t_m(k) + t_m(k) \sum_{P \neq P_0} \exp[-ik(P - P_0)] \{a^{(m)}(P, P_0, k)\} \quad (23)$$

The matrices $a^{(m)}(\mathbf{P}, \mathbf{P}_0, k)$ contain the sum over all possible scattering paths between the first and the last scattering event. They are added to the single scattering amplitude with the appropriate phase factors, but do not themselves depend on the direction of the incoming wave.

This description of the total scattering amplitude is valid in the case of both, an ordered and a disordered crystal, and does not depend (in the latter case) on the way in which the T matrices are averaged. It is not even necessary that an analytic expression exists for the matrices $a(\mathbf{P}, \mathbf{P}', k)$ as it does in the case of an ordered structure, and in this case of a disordered model as well. In our description of the problem the propagator matrices $G_{mn}(\mathbf{P} - \mathbf{P}_0)$ contain an average, that means, they are multiplied by the appropriate probability whenever the distance $\mathbf{P} - \mathbf{P}_0$ is greater than the radius of the configurations shown in fig. 2. The result is a partly averaged T matrix, and the fact that the matrices $a^{(m)}(\mathbf{P}, k)$ do not depend on the direction of the incoming wave is not affected by the averaging procedure. It is also valid in the method applied by Duke and Liebsch [14] who took an average over all possible scattering paths and which results in a single τ matrix for the disordered overlayer.

The invariance with respect to time reversal is now easily shown. Eq. (23) is inserted in (21) and (20) to give

$$\begin{aligned}
 I(\mathbf{k}, \mathbf{k}') = R \langle & \sum_{LL'} Y_{L'}(\Omega_{\mathbf{k}}) \left\{ \sum_{\mathbf{P}} \sum_m e_m(\mathbf{P}) \exp[-i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{P}] t_{LL'}^{(m)}(\mathbf{k}) \right. \\
 & \left. + e_m(\mathbf{P}) t_{LL'}^{(m)*}(\mathbf{k}) \sum_{\mathbf{P}'} \exp[-i\mathbf{k}\mathbf{P}' + i\mathbf{k}'\mathbf{P}] a_{LL'}^{(m)}(\mathbf{P}', \mathbf{P}, k) \right\} Y_{L'}(\Omega_{\mathbf{k}'}). \quad (24)
 \end{aligned}$$

The first term in the sum describes a single scattering event, $t^{(m)}(\mathbf{k})$ is a diagonal matrix, and the product with the spherical harmonics depends on the angle between \mathbf{k} and \mathbf{k}' only. It can be described by $f_m(\vartheta)$. In the second term use can be made of the fact that

$$\begin{aligned}
 Y_{lm}(\vartheta, \varphi) &= (-1)^l Y_{lm}(\pi - \vartheta, \pi + \varphi), \\
 \int Y_{lm}(\Omega) Y_{l'm'}(\Omega) Y_{l''m''}(\Omega) d\Omega \\
 &= (-1)^{l+l'-l''} \int Y_{l'm'}(\Omega) Y_{lm}(\Omega) Y_{l''m''}(\Omega) d\Omega,
 \end{aligned}$$

which leads with the definition of the propagator matrices (eq. (3)) to

$$G_{LL'}(\mathbf{P}) = (-1)^{l+l'} G_{L'L}(-\mathbf{P}). \quad (25)$$

The matrices $a^{(m)}(\mathbf{P}, \mathbf{P}', k)$ contain sums of products of the propagator and t matrices of the following kind:

$$G_{mn_1}(\mathbf{P}_0 - \mathbf{P}_1) t_{n_1} G_{n_1n_2}(\mathbf{P}_1 - \mathbf{P}_2) t_{n_2} G_{n_2n_3}(\mathbf{P}_2 - \mathbf{P}_3) t_{n_3} \dots$$

Using relation (25) in each term of the perturbation series leads to a similar relation for the sum

$$a_{LL'}(\mathbf{P}, P_0, k) = (-1)^{l+l'} a_{L'L}(-\mathbf{P}_0, -\mathbf{P}, k),$$

which means that taking the transpose of the matrix $a(\mathbf{P}, \mathbf{P}', k)$ is equivalent to changing the sign of the lattice vectors \mathbf{P} and interchanging the sequence of scattering events in the perturbation series. Using this relation in eq. (24), it is immediately seen that

$$I(k, k') = I(-k', -k).$$

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