

DIFFUSE LEED INTENSITIES OF DISORDERED CRYSTAL SURFACES

I. Correlations between statistics and multiple diffraction

H. JAGODZINSKI, W. MORITZ and D. WOLF

*Institut für Kristallographie und Mineralogie der Universität München, Theresienstrasse 41,
D-8000 München 2, Germany*

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It is shown that the diffraction of slow electrons from disordered crystal surfaces is correlated with the problem of thermodynamical statistics. The correlation functions are completely determined by the self-energies and interaction energies of neighboring complexes. These quantities solve the problem of a-priori probabilities and the cooperative phenomenon of correlation functions of these complexes. If the calculation of a certain set of multiple scattering amplitudes is possible, the remaining problem of determining the diffuse LEED pattern becomes solvable. The calculation of angular beam profiles follows the same lines as already described for the kinematic theory of X-ray diffraction.

1. Introduction

The successful interpretation of LEED patterns of some crystal surfaces indicates that the approximations used for intensity calculations seem to be valid within the limits of experimental error in present intensity measurements [1–6], the accuracy of which is not extremely good for many reasons. The various theoretical treatments generally lead to a system of linear equations, which may be solved directly in simple cases only [7–9]. Quite a few approximate solutions and iteration procedures have been developed [10–15], treating the multiple scattering within a given layer at the surface exactly, while the multiple scattering between them has to be developed into a perturbation series, which can be done in different ways. Although there are very promising attempts for practical applications, it has to be kept in mind, that a structure determination with variable structural parameters of several atoms in a similar manner as applied for X-ray and neutron-diffraction – or even electron diffraction in the normal range of energy – is still impossible. Consequently, it seems to be hopeless to interpret the LEED patterns of disordered surfaces, which are more frequently realized than ordered ones. This may be concluded from the experimental fact that calculated LEED intensities of

ordered surfaces are about one order of magnitude larger than the observed ones, although they may agree on a relative scale.

In spite of the difficulties mentioned, above we believe that at least a semiquantitative or even a quantitative interpretation of diffuse scattering can be obtained if a specific model for the disorder phenomenon observed has been found.

Recently a theoretical treatment of diffuse scattering, caused by a distribution of defects with pair correlations, has been given by Duke and Liebsch [16]. The restrictions of the applicability of this theory will be discussed in part II.

Apparently all disorder phenomena on crystal surfaces may be described in terms of the two-dimensional Ising model, which has been solved exactly for the simple case of nearest neighbor interactions [17–19]. But this theory is not very well suited to interpret diffraction phenomena, which generally are governed by complicated structural features and can only be described by an extended theory involving a very complicated evaluation. Therefore, computer simulated statistics, according to the so-called Monto Carlo-method, seem to be more promising.

In the following four papers the disorder problem and its influence on LEED will be solved regardless of difficulties arising from computational limitations. For this purpose the contribution of one chain of atoms – extending from the surface into the interior of the crystal - to the diffracted beam is considered to be known (part I). It is shown that this contribution is strongly dependent on the structure of the chain in question and its surrounding, which has to be extended as far as multiple scattering contributes significantly to the scattered intensity (area of multiple scattering). On the other hand, it follows from thermodynamics that the positions of the atoms in a given chain with a certain topological structure are determined by the structures of the surrounding chains. consequently, an area of thermodynamical interaction (ATI) may be defined in a similar way, regulating the free enthalpy of the disordered surface. The correlation between these two areas is discussed in part I, and it is shown that the correlation functions may be derived from the diffraction pattern.

In part II, one possibility of calculating effective scattering amplitudes of a chain embedded in certain surroundings is given. For the sake of rapid convergence, the multiple diffraction with the AMS is calculated accurately, while the influence of the further surroundings is averaged. Although the computational procedures are tedious, a solution is possible at least in simple cases. In spite of the difficulties in quantitatively calculating the scattered intensities, it is often possible to decide between relevant structural models by a statistical consideration of scattered beam intensities or line profiles as a function of energy or diffraction angles. This will be shown later (in some typical examples [26]).

Experimental data of the reconstruction of the (110) surface of Au are dealt with in part III. It is shown that the line profiles are dependent on temperature in a reversible way. The line width of the beam profiles is evaluated with the aid of a simplified deconvolution method.

Finally, an interpretation of the diffraction pictures observed as a function of

temperature is given in part IV, where four different surroundings of the same central chain are introduced with the aid of a stepped surface (micro-terraces on an atomic scale). The theoretical treatment of one-dimensional statistics enables two sequence probabilities to be determined experimentally in terms of the statistical model. So far no comparison has been made with the absolute intensities, but the good agreement between experimental and theoretical line profiles shows that at least the statistical solution is correct.

2. Correlation functions for one-dimensional disorder

Let us describe the geometry of the crystal surface by two translation vectors \mathbf{a} , \mathbf{b} parallel, and \mathbf{c} vertical (or inclined) to the surface; they are determined by the periodic bulk crystal. We consider one chain of unit cells vertical (or inclined) to the surface. The structure of this chain is not necessarily assumed to be periodic, although the lower end is approximately so. Any defect structure may be realized in this chain, each of them corresponding to one configuration. The contribution of this chain to the free energy of the system may be calculated by introducing next, next but one, etc., nearest neighbor interactions, thus defining a complex of chains which determines the structure of the central chain in a first approximation. It is tacitly assumed that a separation of the contribution to a volume and a surface energy is possible. Obviously, a large number of complexes has to be introduced if only a few configurations of the chains are realized and the interaction energies include high-order neighbors, but this is one of the typical features of a surface disorder which cannot be described by a simple statistical theory.

In the case of a one-dimensional approximation for the disorder problem the interaction energies must be strongly anisotropic, such, that one direction shows nearly complete order, while the others do not. In terms of the two-dimensional Ising model [17–19] this approximation should be valid above the critical temperature T_c only with a temperature-dependent chain length L , but one should keep in mind that very often long-range order may not be realized because of relaxation effects below the critical temperature, favouring ordered domains of nearly equal sizes. Thus, a constant chain length parallel to the ordered direction (\mathbf{a}) may often be a reasonable approach to the solution of the problem below T_c . In this particular case the number of configurations is limited as long as the interaction energies may be restricted to second- or third-nearest neighbors.

Let us start with the next-nearest neighbor model: Let the number of configurations of a given chain be limited to m_0 . As has been shown earlier for the kinematic theory, the diffraction problem may be solved if the correlation functions $p_{mn}(j)$ were known. The $p_{mn}(j)$ are the probabilities that a chain at a distance j has the configuration n if, for the reference chain, the configuration m were realized.

According to this definition the following relations exist:

$$p_{mn}(\mathbf{0}) = \delta_{mn}, \quad p_m p_{mn}(j) = p_n p_{nm}(-j),$$

$$\sum_{m=1}^{m_0} p_{mn}(j) = p_n, \quad \sum_{n=1}^{m_0} p_{mn}(j) = 1, \quad \sum_m p_m = 1 \quad (1)$$

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

with $e_{mn}(\mathbf{P}, \mathbf{P}')$ cell occupation operator and $\mathbf{P} = m_1 \mathbf{a} + m_2 \mathbf{b}$, $\mathbf{P}' = m'_1 \mathbf{a} + m'_2 \mathbf{b}$. The a-priori probabilities p_m to find the configuration m for any chain are completely determined by the system of the a-posteriori probabilities $p_{mn}(j)$.

For short-range order we have

$$\lim_{j \rightarrow \infty} p_{mn}(j) = p_n, \quad (2)$$

and in case of long range order a similar relation exists, namely

$$\lim_{j \rightarrow \infty} \sum p_{mn}(j) = p_0^2 p_n \quad (\text{relative probability}), \quad (3)$$

where the summation has to be taken over one superstructure cell (each of them occupied by one chain) containing p_0 subcells, as described by the long-range order. We have introduced eq. (3) only formally, although there is no long-range order (except $T = 0$ K) in the one-dimensional case, which will be treated below.

This discussion shall facilitate the treatment of the two-dimensional disorder problem on the surface, where long-range order may be realized below one or more critical temperatures.

The total potential energy of the infinite one-dimensional crystal surface is given by

$$U = N \left\{ \sum_m p_m \phi_m + \frac{1}{2} \sum_{m,n} [p_m p_{mn}(+1) \phi_{mn}^+ + p_m p_{mn}(-1) \phi_{mn}^-] \right\}, \quad (4)$$

where ϕ_m is the self-energy of the m -th configuration, and ϕ_{mn}^+ , ϕ_{mn}^- are the interaction energies into the positive and negative direction respectively, and N is the total number of cells.

Since $\phi_{nm}^+ = \phi_{mn}^-$ (both represent the same configuration), eq. (4) becomes, on account of eq. (1),

$$U = N \left\{ \sum_m p_m \phi_m + \sum_{m,n} p_m p_{mn}(+1) \phi_{mn}^+ \right\}. \quad (5)$$

It may be shown that the extension of eq. (5) to higher order interactions can be realized simply by introducing complexes of chains as follows:

If the interactions of s neighbors shall be included, complexes of s chains are formed (see fig. 1). We construct the partition function of our one-dimensional

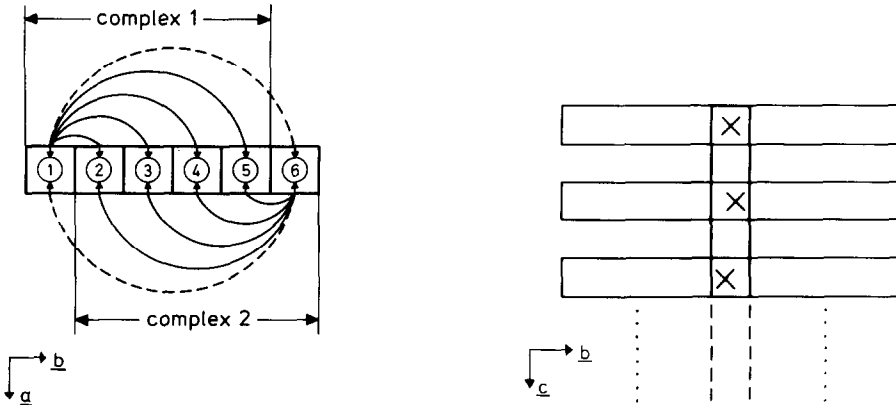


Fig. 1. Self-energies (full line) and interaction energies (broken line) of two adjacent complexes containing 5 chains vertical to the surface. Interactions of $s = 5$ neighbors are counted twice in the energy calculation. In a sequence of complexes each chain appears five times on subsequent complexes, but just once as a central cell. View on the crystal surface.

Fig. 2. Definition of the area of direct thermodynamic interaction (ATI); interactions in and between the inner chain and the indicated area are taken into account. View parallel to the crystal surface (cf. fig. 1).

model with the aid of two overlapping complexes.

The energies – if described by central forces – are counted from the two opposite end chains of the complex; thus all interaction energies are registered twice including the self-energy within the chains, because of the fact that each chain appears twice as “reference” chain in the positive and negative direction respectively. Introducing a new self-energy of binding forces (within the complex) and interaction energies of bonds between the complexes, we can set up a new system of probabilities, which is formally similar to that described by eqs. (1) and (2). From fig. 1, however, it becomes quite clear that the definition of self-energies and interaction energies is arbitrary. There are many possibilities to get another description of the same structural model by interchanging bonds of internal and external interactions (they all should result in the same solution). With this change of the meaning of p_m , ϕ_m , p_{mn} and ϕ_{mn} , eqs. (4) and (5) remain valid.

The major differences of the two solutions are:

- (1) The number of possible “configurations” within a given unit cell is strongly increased.
- (2) The system of probabilities p_m and p_{mn} has completely been changed, such, that neighboring cells may not realize all configurations independently: the occupation of the overlapping unit cells must be the same, which means that a great many probabilities $p_{mn}(j)$ vanish for small values of j .

Now it is easy to generalize this system of probabilities, which is completely

equivalent to the construction of the partition function. Obviously, the calculation of the surface energy has to include *all* structural changes of the atoms near the surface. Therefore, we should not just introduce the upper chain of chains vertical to the surface as indicated in fig. 1, but also take into account the interaction energies caused by structural changes of the substrate layers formed by the above mentioned vertical chains, as shown in fig. 2. Generally speaking, the substrate layer is in equilibrium with the surface layer, which, from a chemical and structural point of view, is different from the bulk crystal. Thus, the chemistry and the atomic position should also be different, causing a change in energy even in the deeper part. These changes are due to the interactions between the complex at the surface and the interior. Applying the above mentioned kind of counting to bonds, we get a new set of self-energies and interaction energies, now describing the contribution of one atom, and the structural dependent set of atoms below this atom, to the energy of the surface. The total area of interaction is $(s + 1)d$ where d is the interaction depth between surface and inner atoms. Let us define this area as the "area of direct thermodynamical interaction" (ATI). Extending this model to the two-dimensional surface, the interaction length L , vertical to this direction, has to be considered separately. The volume of interaction is then $(s + 1)dL$. It is tacitly assumed that equal complexes of the surface layer cause the same structures, or at least very similar ones, of the adjacent substrate layers which are apparently very similar to the periodic arrangement of the bulk crystal, but naturally different from the surface layer which generates the distortions of the deeper layers formed by the lower end of the chains parallel to c . If there are small fluctuations in this structure, the potential energy within the ATI has to be replaced by a free energy $F = \Phi - TS$, including the entropy of this area. But we have to keep in mind that the entropy term TS is also correlated with the vibrational term of energy. Thus, TS describes the change in internal heat and potential energy due to a configurational entropy within the ATI. This is clearly a very crude approximation, but at the moment it is useless to try a more accurate approach, because it seems to be impossible to calculate the surface modes and the change of internal vibrational modes of a partly ordered surface accurately. This approximation means that the surface modes and the change of the internal modes are calculated with the aid of the accurate binding forces within the ATI and averaged binding forces originating from the atoms of the area outside the ATI. Now the calculation of the $p_{mn}(j)$ is correlated with the construction of the partition function Z of the system. We introduce the free energy

$$F_{mn} = \bar{F} + \Delta F_{mn}(j),$$

which determines the Boltzmann factor $b_{mn} = \exp(-F_{mn}/kT)$ in the partition function. Now we can define the "partial" partition function $p_{mn}(j)$ of $j + 1$ chains starting with the configuration m and ending with n ; we get the following recursion formula

$$Z_{mn}(j + 1) = \sum_l Z_{ml}(j) b_{lm}. \quad (6)$$

Eq. (6) means that the construction of the partition function can be done without any difficulty. The partial partition functions are considered to be vector components, such, that the increase of the number of chains by one can be done by matrix multiplication, with the matrix B containing the Boltzmann factors.

The partition function Z of a surface containing N_0 chains is then given by the sum of all elements of the matrix B^{N_0} :

Introducing

$$\bar{F} = \frac{1}{m_0} \sum_{m,n} F_{mn} \quad \text{and} \quad F_{mn} = \bar{F} + \Delta \bar{F}_{mn},$$

with

$$\sum_{m,n} \Delta F_{mn} = 0, \quad m_0 = \text{number of complexes}, \quad b_{mn} = \exp(-\Delta F_{mn}/kT),$$

we get

$$B^j = \exp(-jF/kT) \Delta B^j. \tag{7}$$

Eq. (7) may be solved with the aid of the eigenvectors and eigenvalues of the matrix ΔB .

As mentioned above each element of the matrix B^j describes the relative probabilities of a partial partition function, starting with the element m and ending with an element n . The sum over all elements of B gives the partition function of a system containing j elements. For the diffraction problem the absolute probabilities are needed, which can easily be determined by replacing the Boltzmann factors b_{mn} by absolute probabilities.

$$\alpha_{mn} = b_{mn} / \sum b_{mn} \tag{8}$$

The calculation of the α matrix is necessary, where α_{mn} is the probability $p_{mn}^{(+1)}$ as defined in eq. (1). Let U be the matrix which diagonalizes α , we get:

$$\begin{aligned} \alpha^j &= U^{-1}(U\alpha U^{-1})(U\alpha U^{-1}) \dots (U\alpha U^{-1}) U \\ &= U^{-1} \alpha^j U \\ &= U^{-1} \begin{pmatrix} \lambda_1^j & 0 \\ 0 & \lambda_m^j \end{pmatrix} U. \end{aligned} \tag{9}$$

Eq. (9) means that the elements of the matrix α^j may be expressed by the eigenvalues λ_i of the α matrix.

The general solution of the probabilities has now been solved:

$$p_{mn}(j) = \sum_{i=1}^{m_0} C_{mni} \lambda_i^j, \tag{10}$$

where the C_{mnji} are given by the boundary conditions and may be calculated in various ways [20]. Before starting the discussion on the applicability of eq. (10) for the two-dimensional Ising-model on real crystal surfaces, we shall first discuss the multiple diffraction problem.

3. The diffraction problem

Let us now define the area of multiple scattering, AMS, which seems to be important in cases, where the cross sections for elastic and inelastic scattering are sufficiently large. Fig. 3 shows the main principles: Both, the incident and the scattered electron, are described by plane waves with the wave vectors k, k' . The surface of the crystal is subdivided into unit cells as described by the lattice vectors a, b at the surface. Within the unit cell there shall be one chain of atoms only, vertical (or nearly vertical) to the surface. We consider the contribution of this chain to the scattered electron as last process of the multiple scattering. This contribution to the plane wave of the scattered electron depends:

- (a) on the structure of the chain;
- (b) on the position of the chain relative to the idealized surface;
- (c) on the arrangement of an area of finite size surrounding this chain, let us call this "area of multiple scattering" (AMS).

The AMS as defined under (c) may be equal, larger or smaller than the ATI. Generally it is less anisotropic than the ATI considered here, because of multiple scattering, which covers all directions of the crystal. Let us first discuss the mathematical treatment of cases, where the AMS is equal to the ATI. For disordered sur-

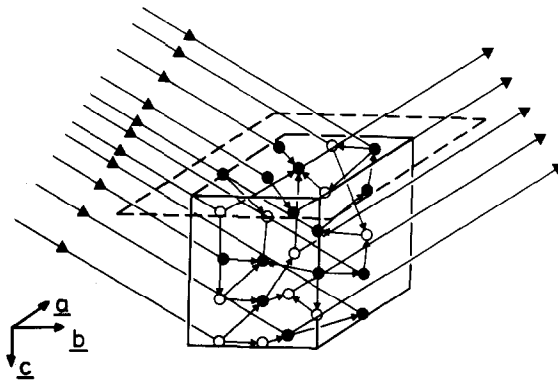


Fig. 3. Definition of the area of multiple scattering (AMS). All multiple scattering processes within the given area are calculated exactly, while the remaining ones outside that area are averaged. For the solution of the diffraction problem the contribution of the central chain only is needed.

faces it is convenient to introduce three-dimensional reciprocal vectors a^* , b^* , c^* with

$$h = ha^* + kb^* + lc^*$$

where c^* is vertical to the crystal surface. However, there are some difficulties for a^* and b^* , if the chains have not been chosen vertically.

This effect may be taken into account by an appropriate calculation of the scattering amplitude of the AMS; so we may assume c^* to be vertical, and a^* and b^* parallel to the surface. Introducing $F_m(k, k')$ as scattering amplitude of a chain in the m -th configuration in the AMS, and $r_m(P)$ describing the position of the chain in the m -th configuration in the cell at point P of the lattice:

$$P = m_1a + m_2b, \quad r_m(P) = P + \Delta r_m(P). \quad (11)$$

Now the scattering amplitude of an electron leaving the surface is

$$A(k, k') = \sum_{P,m} F_m(P)(k, k') \exp(2\pi i h \cdot r_m(P)). \quad (12)$$

In case of an ordered lattice, where the scattering of all unit cells is equal (only one F_m and one displacement vector r_m), we get:

$$\begin{aligned} A(k, k') &= \sum_m F_m(k, k') \exp(2\pi i h \cdot \Delta r_m) \frac{\sin \pi N_1 h}{\sin \pi h} \frac{\sin \pi N_2 k}{\sin \pi k} \\ &= \sum_m F_m(k, k') \exp(2\pi i h \cdot \Delta r_m) \sum_g \delta(h - g), \end{aligned} \quad (13)$$

where

$$h = ha^* + kb^* + lc^* = k - k', \quad g = h_0a^* + k_0b^*,$$

and h_0 and k_0 are integers.

The calculation of the scattering amplitude $F_m(k, k')$ follows the same lines as described in the literature, where the AMS is extended to infinity. In the case of a disordered lattice it is useful to replace $F_m(P)$ in eq. (12) by

$$F_m(P) = \bar{F} + \Delta F_m(P), \quad (14)$$

with

$$\bar{F} = \frac{1}{m_0} \sum_{m=1}^{m_0} p_m F_m \exp(2\pi i h \cdot r_m(P)).$$

Inserting (14) into eq. (12) and summing up partially, we get

$$\begin{aligned} A(k, k') &= \bar{F} \sum_g \delta(h - g) \\ &+ \sum_{P,m} \Delta F_m(P) \exp(2\pi i h \cdot \Delta r_m(P)) \exp(2\pi i h \cdot P) \\ &= G(k, k') + D(k, k'). \end{aligned} \quad (15)$$

In principle we get the same result as known in the kinematic diffraction theory; the only difference is that we have to average over multiple scattering amplitudes, the calculation of which causes some difficulties. It has also been assumed that the displacement vector $\Delta r_{m(P)}$ is determined by the configuration only and is independent from the surrounding, but there may be a displacement into the c -direction, depending on the statistical solution of the problem: therefore the sequence of two configurations may be correlated with a displacement parallel c . We shall show in a later paper that a general configuration-dependent displacement vector parallel to the surface may be treated according to the so called theory of "satellites" [24,25], the inclusion of which results in the existence of satellite reflections, accompanying the main reflections. Consequently our theory is limited to diffraction patterns where satellites are missing.

According to eq. (15) the scattered intensity is given by

$$AA^* = |A|^2 = G^2 + 2 \operatorname{Re} GD + |D|^2. \quad (16)$$

The two first terms in eq. (16) contribute to sharp reflections only, while $|D|^2$ may generate sharp and/or diffuse reflections, depending on the state of order on the surface.

For calculating the diffuse intensity it is more convenient to form $|A|^2$ with the aid of eq. (12):

$$|A|^2 = \sum_P \sum_{P'} F_m(P) F_m^*(P') \exp[2\pi i l (\Delta r_{m(P)} - r_{m(P')})] \\ \times \exp 2\pi i h \cdot (P - P'), \quad (17)$$

Setting $P' = P + j$ with $j = j_1 a + j_2 b$ and $P - P' = -j$, we can replace the products

$$F_m(P) \exp(2\pi i l \Delta r_{m(P)}) F_m^*(P+j) \exp(2\pi i l r_{m(P+j)}), \quad (18)$$

by average values, which may be obtained with the aid of p_m and $p_{mn}(j)$. The complex factors $\exp(2\pi i l \Delta r_{m(P-P')})$, etc. have to be determined by introducing complex sequence and a-posteriori probabilities. This can be done by adding to the sequence probabilities the phase factors in such a way that $p_{mn}(j)$ does not only give the a-posteriori probability of the n -th configuration in the cell (reference cell) — being $j_1 a + j_2 b$ apart from the original cell — but also its complex factor to be added to the probability calculated. Consequently, new complex functions $p'_{mn}(j)$ are introduced, which may be calculated in a similar manner as described above for the real probabilities. This procedure will be explained with the aid of a special example in Part IV of this series of papers.

Thus, the average products given in (18) may be calculated:

$$\langle F_P F_{P+j}^* \exp(2\pi i l \Delta r_{m(P-P')}) \rangle = p_m F_m p'_{mn} F_n^* \quad (19)$$

Introducing this result in eq. (17), we get [23]

$$|A|^2 = \sum_{j_1, j_2} \sum_{m, n} [(N_1 - |j_1|)(N_2 - |j_2|) p_m p'_{mn} \times F_m F_n^* \exp(-2\pi i \mathbf{j} \cdot \mathbf{h})] . \tag{20}$$

Introducing

$$p'_{mn}(\mathbf{j}) = p_n + d_{mn}(\mathbf{j}) ,$$

one part of the summation can be done, and we get

$$|A|^2 = N_1 N_2 \sum_{m, n} p_m p_n^* F_m F_n^* \sum_{\mathbf{g}} \delta(\mathbf{h} - \mathbf{g}) + \text{rest} \\ = N_1 N_2 \left| \sum_m p_m F_m \right|^2 \sum_{\mathbf{g}} \delta(\mathbf{h} - \mathbf{g}) + \text{rest} . \tag{21}$$

Eq. (21) describes the behaviour of sharp reflection, the intensity of which is given by an averaged generalized structure factor of similar structure as known for the kinematic diffraction theory.

In order to study the behaviour of diffuse scattering, we return to eq. (20). Neglecting j_1 and j_2 which are small compared to N_1 and N_2 , we get

$$|A|^2 = N_1 N_2 \sum_{m, n} \sum_{j_1, j_2} p_m p'_{mn}(j_1, j_2) F_m F_n^* \exp(-2\pi i \mathbf{j} \cdot \mathbf{h}) . \tag{22}$$

Setting

$$p'_{mn}(\mathbf{j}) = w_{mn}(\mathbf{x}') \delta(\mathbf{x}' - \mathbf{j}) , \quad \mathbf{x}' = \mathbf{x}a + \mathbf{y}b ,$$

where w_{mn} are the “smoothest” continuous curves passing through all points of the corresponding p'_{mn} , we can replace the summation in eq. (22) by the integral and get

$$|A|^2 = N_1 N_2 \sum_{m, n} p_m \left[\int w_{mn}(\mathbf{x}') \sum_{\mathbf{j}} (\mathbf{x}' - \mathbf{j}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x}') d\mathbf{x}' \right] F_m F_n^* .$$

The expression in square brackets represents the Fourier transforms of a sum of product functions, which, after evaluation of the integral, become a sum of convolution with the Fourier transforms of the w and δ functions:

$$|A|^2 = N_1 N_2 \sum_{\mathbf{g}} \delta(\mathbf{h} - \mathbf{g}) \overbrace{\sum_{m, n} p_m W_{mn}(\mathbf{h})} F_m F_n^* , \tag{23}$$

where $W_{mn}(\mathbf{h})$ are the Fourier transforms of the continuous probability functions $w_{mn}(\mathbf{x}')$. The arc represents the convolution operation. The sum of the δ functions in reciprocal space results in the two-dimensional reciprocal lattice parallel to the surface. These functions are smeared out by the variety of Fourier transforms of

the ordering functions multiplied by the complex structure factors, which may be calculated approximately according to the method described in part II. Although eq. (23) has the same structure as has been derived in the kinematic theory of diffraction, the calculation of $F_m(\mathbf{k}, \mathbf{k}')$ is much more difficult and needs a specific computer program (see part II). As the number of F_m increases with the complexity of the problem in question, the possibility of calculating complicated problems is limited by the size of the present day computers.

If the ATI is larger than the AMS, an equal contribution to the scattering amplitudes of complexes with the same SMS causes no difficulty. But we should add some few remarks for examples with a larger AMS. In principle it should be possible to calculate the a-priori and a-posteriori probabilities by formally extending the ATI to the size wanted. According to eqs. (9) and (10) the rank of the matrix α and the number of characteristic values λ_i should increase considerably. However, it may easily be shown that these additional λ are identical with those already given for the ATI, and consequently, the problem becomes degenerate. How this difficulty can be solved can best be shown for special examples. The probabilities of the new complexes are obtained by expanding the simple old probabilities into the new ones with the aid of the sequence probabilities of immediate neighbours used in the original solution.

Eqs. (22) and (23) may also be applied to the one-dimensional case of disorder, with small changes of the symbols used. As the summation over the ordered direction \mathbf{b} can be carried out, the F_m, F_n now represent the scattering of a finite array of chains.

Eq. (23) reads then

$$|A|^2 = \frac{\sin^2 \pi N_2 k}{\sin^2 \pi k} \sum_{\mathbf{h}_0} \delta(\mathbf{h} - \mathbf{h}_0) \sum_{m,n} p_m W_{mn}(\mathbf{h}) F_m F_n^*, \quad (24)$$

where $\mathbf{h}_0 = \mathbf{h}_0 \mathbf{a}^*$.

According to eqs. (23) and (24), the $W_{mn}(\mathbf{h})$ are the Fourier transforms of $w_{mn}(\mathbf{x}')$, which are defined in the \mathbf{x}' space as the smoothest curves passing through the points of $p'_{mn}(\mathbf{j})$. This function is defined for integers j_1, j_2 only. In order to guarantee a rapid convergence and a "simple" behavior, it is sometimes advisable to subdivide $p'_{mn}(\mathbf{j})$ into a sum of functions, fulfilling this condition in a better way. This is generally the case if there is more than one position in the unit cell, not being symmetrically equivalent. In this case it is advisable to replace $p_{mn}(\mathbf{j})$ by

$$p'_{nm}(\mathbf{j}) = \sum_{\nu, \mu} p'_{mn|\nu\mu}(\mathbf{j}) \quad \text{and} \quad p_n = \sum_{\nu} p_{n|\nu}, \quad (25)$$

where ν and μ are site indices in the original and reference cell.

It is also convenient to introduce a general phase factor for the position parameters x, y and z of the ν -th site in the cell. As we use one position parameter only, this formal difficulty need not be considered here.

We shall now give the evaluation of eq. (22) for the one-dimensionally disordered surface by calculating $p'_{mn}(j)$. According to eq. (10), these probabilities are given by

$$p_n p'_{mn}(j) = \sum_i C_{mn|i} \lambda_i^j.$$

Inserting this expression into eq. (22) and considering (24), we get:

$$\begin{aligned} |A(\mathbf{k}, \mathbf{k}')|^2 &= N_1 \frac{\sin^2 \pi N_2 h}{\sin^2 \pi h} \sum_j \sum_{m,n} p_n p'_{mn}(j) F_n F_m^*(\mathbf{k}, \mathbf{k}') \exp(-2\pi i j k) \\ &= N_1 \frac{\sin^2 \pi N_2 h}{\sin^2 \pi h} \sum_i \left[\sum_{m,n} C_{mn|i} \sum_j \lambda_i^j \exp(-2\pi i j k) \right] F_n F_m^*(\mathbf{k}, \mathbf{k}') \\ &= N_1 \frac{\sin^2 \pi N_2 h}{\sin^2 \pi h} \sum_i K_i(\mathbf{k}, \mathbf{k}') \sum_j \lambda_i^j \exp(-2\pi i j k). \end{aligned} \tag{26}$$

Replacing K_i and λ_i by

$$K_i(\mathbf{k}, \mathbf{k}') = B_i(\mathbf{k}, \mathbf{k}') + iD_i(\mathbf{k}, \mathbf{k}') \quad (B_i, D_i \text{ real quantities}),$$

$$\lambda_i = \rho_i \exp(2\pi i \varphi_i),$$

the geometrical series of eq. (26) may be figured out as

$$\begin{aligned} |A|^2 &= N_1 \frac{\sin^2 \pi N_2 h}{\sin^2 \pi h} \left[\sum_i B_i \frac{1 - \rho_i^2}{1 - 2\rho_i \cos 2\pi(k - \varphi_i) + \rho_i^2} \right. \\ &\quad \left. - 2D_i \rho_i \frac{\sin 2\pi(k - \varphi_i)}{1 - 2\rho_i \cos 2\pi(k - \varphi_i) + \rho_i^2} \right]. \end{aligned} \tag{27}$$

The denominator of both terms in eq. (27) has minima if

$$\cos 2\pi(k - \varphi_i) = 1.$$

The real part B_i generates a symmetric and the imaginary part D_i an antisymmetric contribution to the reflection profile. Each λ_i produces a different peak as long as all λ_i are different. $|\lambda_i| = 1$ generates a sharp and $|\lambda_i| = 0$ a completely diffuse reflection.

The functions B_i and D_i are strongly dependent on multiple diffraction and may vary considerably with \mathbf{k} and \mathbf{k}' , but as long as the reflections are well defined (sufficiently ordered) changes in intensity may be taken into account by calibration of the peak intensity and the asymmetric contribution (see parts II and IV). From this consideration we may conclude that the eigenvalues of the α -matrix exhibit a very important property: each of them defines one diffuse reflection in the diffraction pattern, the line width of which is determined by ρ_i , while the position is given by φ_i .

This behaviour of the intensity enables the application of eq. (27) in another

way, ρ_i and φ_i are determined experimentally, and a model of disorder is suggested which yields the correct values for them.

As has been pointed out above, the chains introduced are not described by their potential energies alone, they have to include at least some dynamic disorder, caused by the change of vibration spectra of the chains. The sequence probabilities, which should be temperature-dependent because of the one-dimensional treatment, are defined by

$$\alpha_{mn}(T) = \exp[-L(T) \Delta F_{mn}/kT] \left\{ \sum_{m,n} \exp[-L(T) \Delta F_{mn}/kT] \right\}^{-1}, \quad (28)$$

where $L(T) = N_2$ (eq. (26)) is the average number of unit cells belonging to one chain. The average chain length $L(T)$ is heavily influenced by the back-coupling of the probabilities α_{mn} , such that a stronger correlation results in an increase of $L(T)$. This back-coupling effect is necessary for the existence of a critical temperature T_c , where $L(T_c)$ becomes infinite. $L(T_c)$ is practically limited for various reasons (finite crystal relaxation effects, anti-phase domains, etc.) In this particular case $L(T)$ becomes large but independent from T below the critical temperature T_c , which loses its real critical character. It is this range of temperature where eq. (28) may be applied successfully without major restrictions, but it should be pointed out that this approximation is of limited validity. An application will be given in part IV.

4. Two-dimensional disorder

In a more exact treatment $L(T)$ has to be replaced by a solution in two dimensions, which is completely different from the one-dimensional one, though the construction of the partition function may be done in a very similar way. Two major differences shall be described briefly.

(1) The decrease of correlations as a function of the distance vector j was proportional to $|\lambda_i|^{|j|}$. This property changes in two-dimensional cases for two reasons:

(a) The correlation function should be anisotropic because of the shape effect of ordered areas, which is meaningless in the one-dimensional case,
 (b) the damping law of correlation functions changes because of the back-coupling, a better description may be $|\lambda_i|^{|j|^r}$, where r is dependent on the dimension ($r = 1$ for the one-dimensional case).

(2) The number of configurations increases considerably if the restriction to nearest neighbor interactions is released. This increase causes a great variety of characteristic values $\lambda_i = \rho_i \exp(2\pi i \varphi_i)$, describing the periodicities of the structure. This fact is responsible for many anomalies in the diffraction picture.

All equations given in the preceding sections which are not yet extended to the general two-dimensional case of disorder may be generalized. Although the so-called two-dimensional Ising model should be applicable to any surface disorder, the limitation to interactions of next nearest neighbors is so imposing that a real

quantitative application seems to be impossible. There are apparently two possibilities to overcome these difficulties:

- (1) to analyze the Fourier-transforms W_{mn} directly;
- (2) to construct the probabilities p_{mn} directly by a computer simulation of the partial partition functions.

It is clear that the first method can be applied only if the number of functions W_{mn} is small enough, in order to isolate them for a general interpretation. The observed averaged function which can be derived directly from the diffuse reflection cannot easily be separated because of the existence of phase differences between the W_{mn} , they are due to the structure factors of complexes, which contain phase shifts due to the various atomic positions or to displacement vectors involved statistically. If there are various positions in the cell, participating in the disorder, it is practical to introduce the site-dependent correlation function $p_{mn/\mu\nu}(\mathbf{f})$ which refer to the ν -th site in the original and the μ -th site in the reference cell, cf. eq. (25). These functions may show a less complex behavior as far as their damped periodicities are concerned.

The second possibility has been treated for the three-dimensional [21] and the two-dimensional case as well [22]. It is applicable if there is a clear idea of the disorder model realized. Therefore, it is first necessary to give a qualitative picture of the disorder model by interpreting the Fourier transforms of the correlation functions. Subsequently, a quantitative approach to the diffuse scattering can be done.

5. Conclusions

The calculation of diffuse intensities scattered by disordered surfaces is very difficult in cases where the area of multiple scattering is sufficiently large. A great many configurations have to be considered, and computer time spent on the evaluation of multiple scattering processes on each one of the matrices is not warranted, nor technically possible. With increasing order the number of possible configurations decreases very rapidly on account of the fact that a great number of configurations have low a-priori probabilities. Near the critical temperature a consistent set of configurations is sufficient for a quantitative description of the diffraction picture.

One of the most important omissions of this theory (and all others) is the crude approximation of the absorption introduced. It may be shown that a variable absorption field introduced into the scattering amplitude of multiple scattering does not change the principles of this approximation, but the difficulties in calculating the $F_m(k, k')$ increase considerably.

The LEED problem of disordered surfaces is essentially the same as already described for the kinematic theory of diffraction. It is the quantitative interpretation only that causes a great many difficulties. However, we may expect that the

experience available from X-ray diffraction may contribute at least qualitatively to the interpretation of LEED patterns of disordered surfaces.

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