LOW ENERGY ELECTRON DIFFRACTION
BY THIN FILMS
PART I

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A simple dynamical approach to the description of the low energy electron diffraction (LEED) intensity is presented using the quantum field methods developed in thin film theories [1, 2, 5]. The scattering amplitude of the electrons scattered by the metallic thin film is expressed in terms of the surface electron density modulated by lattice vibrations of the atoms at the surface.

The influence of the temperature on the thin film dynamics and then on the LEED intensity is treated in pseudoharmonic approximation [4, 5]. The pseudoharmonic approximation brings an essential correction to the temperature behaviour of LEED spectra, and the approximation can be useful to study the change of the lattice parameters of the film, in particular near the surface.

1. Introduction

Until now the chief motivation for the study of LEED intensities has been the possibility of determining crystal surface structure by intensity analysis in a way analogous to the determination of crystal bulk structure by X-ray diffraction. A common feature of any method of structure determination by diffraction is the possibility to calculate the diffraction intensity for a known structure. This problem, however, in the case of LEED is very difficult that has not yet been treated with the accuracy necessary for structure determination. The difficulties stem mainly from the circumstance that low-energy electrons in crystals suffer very strong scattering, bot elastic and inelastic.

Most attempts to account for the regularities in the energy dependence of the LEED intensity curves involve the calculation of the multiple scattering of electrons between atoms and between atomic layers of the crystal. The general theory of LEED which includes all orders of multiple scattering is called dynamical theory and is practically synonymous with band theory. The results of the dynamical theory of LEED are presented with reference to the band structure of the crystal. One approach to the dynamical theory of LEED intensity which is currently in wide use is nearly free electron treatment due orginally to Bethe [3]. In this theory the scattering power of a crystal is represented by Fourier components U_g of its potential. The zeroth term U_0, the inner potential, causes an overall shift of the band structure to lower energies, while

the higher order terms, U_g are responsible for the band gaps. Apart from the general displacement by U_0, the top edge of each band gap for an attractive potential coincides with a Bragg condition and the width of the gaps $2U_g$, where g is the reciprocal lattice vector included in the Bragg condition.

Recently considerable progress has been made in the understanding of the origin of the major features in LEED intensity data and the required dynamical theory has been developed to a point where it can make predictions that may be tested by experiments. However, in addition to being quite complex, the theory is still incomplete, and as a result it has not yet become a practical tool that can be used routinely in the interpretation of structures from experimental data.

In the present paper we give a modified approach to the description of the LEED intensity by means of the methods developed in thin film theories [1, 2]. A scattering sample is treated as a thin film evaporated on substrate. In this way we introduce into consideration of the LEED in a natural way the free surface of the sample which plays a very important role in the problem. We describe the temperature dependence of the surface effects considered in the low energy diffraction introducing a dynamical scattering potential which is a temperature and thickness dependent quantity. The dynamics of the thin film lattice particles are described using the anharmonic model of the thin film crystal in the pseudoharmonic approximation elaborated for bulk crystals in [4] and for thin films in [5]. Using the pseudoharmonic approximation one can explain the temperature dependence of the energy shift of the Bragg peaks, which are due to the change of the lattice distance between atoms and layers, as well as the temperature behaviour of the LEED intensity.

2. Heterogeneity of the scattering potential of a sample with a surface

We shall assume that the experiment has been sufficiently well prepared to consider a monoenergetic, collimated beam of electrons incident on a perfectly clean, well ordered surface of the sample. Our interest will centre on the elastically scattered electrons, because they produce almost all the structure in the diffraction pattern. We divide the scattering sample into a thin film and a substrate. By the thin film we will understand n monoatomic layers parallel to the surface and we number them by v beginning with $v = 1$ for the free surface of the film and finishing with $v = n$ for the atomic layer which is lying directly on the substrate. We denote the atomic positions inside a v-th layer of the film by the two dimensional vector $\mathbf{J}$ and the distance between two atomic sites in the thin film by vector $\mathbf{R}_{vj}$.

The physical motivation of the model we chose is as follows. The surface atoms of any solid body are in a situation which is different from that of atoms situated in the inside of the material. The surface atoms feel the changes in the geometry of the neighbours surrounding them caused by the missing neighbours, by the spontaneous deformation of the lattice near the surface. As a result the scattering potential near the

surface must be different from that inside of a bulk material. It is to be expected that the changes of the electronic structure near the surface must cause some changes of all physical properties related to the surface. The redistribution of the electrons near the surface creates some new boundary conditions for lattice vibrations which must influence the temperature-dependence of the low energy electron diffraction intensity, because the low energy electrons in LEED experiments are mainly scattered by a field near the surface of a sample.

To describe the scattering potential $V(r)$ for LEED we suppose that in a static case it can be written as a sum of atomic potentials $V_0(\mathbf{r} - \mathbf{R}_{vj})$ produced by all atoms of the considered film in the presence of the substrate, that is, we suppose that

$$V(\mathbf{r}) = \sum_{vj} V_0(\mathbf{r} - \mathbf{R}_{vj}). \tag{1}$$

We consider the atomic potential as a sum of the potentials produced by the electrons at the free atom orbitals κ, where κ denotes a set of the quantum numbers for free atom electrons. The potential of a free atom at rest $V_0(\mathbf{r})$ can be expressed by

$$V_0(\mathbf{r}) = -\frac{Ze^2}{r} + \sum_{\kappa} \int \frac{e^2 \rho_{\kappa}^0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r', \tag{2}$$

where (Ze^2/r) is the Coulomb potential of the nucleus, ρ_{κ}^0 denotes the electron density distribution of the κ-th orbital, which can be taken for a free atom in the form [6]:

$$\rho_{\kappa}^0(r) = \alpha_{\kappa} e^{-\beta_{\kappa} r}, \tag{3}$$

where α_{κ} and β_{κ} are the numerical parameters which can be found by means of the method presented in [6].

In thin films, however, different atoms are in different circumstances, as we mentioned above, so the electron density distribution of the κ-th orbital may change from one atom to another, particularly, in the direction perpendicular to the surface of the film. Taking into consideration the above statement we propose the following expression for the electron distribution in the (vj)-th atom of thin film, namely

$$\rho^0(\mathbf{r} - \mathbf{R}_{vj}) = \sum_{\kappa} \langle n_{vj\kappa} \rangle \rho_{\kappa}^0(\mathbf{r} - \mathbf{R}_{vj}), \tag{4}$$

where $\langle n_{vj\kappa} \rangle$ denotes the effective numbers of electrons at the κ-th orbitals of the vj-th atom, which can be found in a self-consistent way in which the boundary conditions at the surface are taken into account [2]. In this way the static scattering potential for the electrons diffracted by thin film can be written in the general form [6]

$$V_0(r) = -\sum_{vj} \left\{ \frac{Ze^2}{|r - \mathbf{R}_{vj}|} - \sum_{\kappa} e^2 \langle n_{vj\kappa} \rangle \int \frac{\alpha_{\kappa} e^{-\beta_{\kappa}|\mathbf{r} - \mathbf{R}_{vj} - \mathbf{j}'|}}{|\mathbf{r} - \mathbf{R}_{vj} - \mathbf{r}'|} d^3 r' \right\} =$$

$$= -Ze^2 \sum_{vj\kappa} \alpha_{\kappa} \langle n_{vj\kappa} \rangle \frac{e^{-\beta_{\kappa}|\mathbf{r} - \mathbf{R}_{vj}|}}{|\mathbf{r} - \mathbf{R}_{vj}|}, \tag{5}$$

where e stands for electron charge. It is known, however, that even at zero temperature the atoms of the sample take part in their temperature vibrations around their equilibrium position, and the influence of the temperature on the scattering potential of the real sample must be taken into consideration. In the present paper the influence of the temperature on the scattering potential we take into consideration defining the dynamic scattering potential $V_T(\mathbf{r})$ for (vj)-th atom in a thin film as

$$V_T(\mathbf{r} - \mathbf{R}_{vj}) = \left(\frac{1}{2\pi B_{vj}}\right)^{3/2} \int V_0(\mathbf{u} - \mathbf{R}^0_{vj}) e^{-\frac{|\mathbf{r} - \mathbf{R}^0_{vj} - \mathbf{u}|^2}{2B_{vj}}} d^3 u, \tag{6}$$

where $\mathbf{R}^0_{vj}$ denotes the equilibrium position of the atom under consideration, B_{vj} denotes its mean square displacement from the equilibrium position and the function $T(r) = (2\pi B_{vj})^{-3/2} e^{-\frac{u^2}{2B_{vj}}}$ is used as the temperature-dependence distribution of the mass centre of the atom in thin film during its vibration around the equilibrium position [7]. Then the full temperature-dependent scattering potential for the film can be taken in the form [9]

$$V_T(r) = -Ze^2 \sum_{vj} \left(\frac{1}{2\pi B_{vj}}\right)^{3/2} \int \frac{e^{-\frac{|\mathbf{r} - \mathbf{R}^0_{vj} - \mathbf{u}|^2}{2B_{vj}}}}{|\mathbf{u} - \mathbf{R}^0_{vj}|} d^3 u +$$

$$+ \sum_{vjk} e^2 \langle n_{vjk} \rangle \int d^3 r' \int d^3 u \left(\frac{1}{2\pi B_{vj}}\right)^{3/2} \alpha_k \frac{e^{-\beta_k |\mathbf{r}' - \mathbf{R}_{vj}|}}{|\mathbf{u}' - \mathbf{R}_{vj} - \mathbf{r}'|} e^{-\frac{|\mathbf{u} - \mathbf{R}^0_{vj} - \mathbf{r}'|^2}{2B_{vj}}}. \tag{7}$$

After the integration [9, 10] we obtain the following useful expression

$$V_T(\mathbf{r}) = +Ze^2 \sum_{vjk} \frac{\alpha_k \langle n_{vjk} \rangle}{|\mathbf{r} - \mathbf{R}^0_{vj}|} e^{\frac{\beta_k^2 B_{vj}}{2}} F_k(|\mathbf{r} - \mathbf{R}^0_{vj}|), \tag{8}$$

where

$$F_k(|\mathbf{r} - \mathbf{R}^0_{vj}|) = e^{-\beta_k |\mathbf{r} - \mathbf{R}^0_{vj}|} \left[1 - \Phi\left(\beta_k \sqrt{\frac{\beta_{vj}}{2}} - \frac{|\mathbf{r} - \mathbf{R}^0_{vj}|}{\sqrt{2\beta_{vj}}}\right)\right] -$$

$$- e^{+\beta_k |\mathbf{r} - \mathbf{R}^0_{vj}|} \left[1 - \Phi\left(\beta_k \sqrt{\frac{\beta_{vj}}{2}} + \frac{|\mathbf{r} - \mathbf{R}^0_{vj}|}{\sqrt{2\beta_{vj}}}\right)\right] \tag{9}$$

and

$$\Phi(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt. \tag{10}$$

This form of the scattering potential has interesting properties. At first this potential is finite at every lattice point $\mathbf{R}^0_{vj}$, contrary to the effective potential of the free atoms which is infinite at the middle of the atom. An other thing we point out is that for $B_{vj} = 0$ it comes back to the static form (5). In the next Section we use this form of the dynamical potential to calculate the temperature dependence of the low energy electron amplitude.

3. Determination of the scattering amplitude for the LEED experiments

The scattering potential in the heterogeneous system derived in the last Section is used now to calculate the amplitude of the scattering of the electrons by thin film for the LEED experiments. To obtain an expression for the scattering amplitude there are possible approximation schemes which are essentially reduced to two alternatives. One consists of a power series expansion in the strength of the potential which can be generated as follows, starting from the integral equation for the wave function of the diffraction problem

$$\psi_k(\mathbf{r}) = \left(\frac{1}{2\pi}\right)^{3/2} e^{i\mathbf{k}\mathbf{r}} - \frac{1}{4\pi} \int \frac{e^{\pm i\mathbf{k}(\mathbf{r}-\mathbf{r}')}}{|\mathbf{r}-\mathbf{r}'|} V_T(\mathbf{r}')\psi_k^{\pm}(\mathbf{r}')d^3r' =$$
$$= \varphi_k + \int G_0(\mathbf{r},-\mathbf{r}')V_T(r')\psi_k^{\pm}(\mathbf{r}')d^3r' \tag{11}$$

and solving it by iteration for the $V_T(\mathbf{r}')$ potential we thus obtain, omitting the index $\pm$ for brevity, $\psi_k^0 = \varphi_k$, where $\mathbf{k}$ denotes the wave vector of the incident electron and φ_k is simply its plane wave. Using this on the right-hand side of Eq. (11) we have:

$$\psi_k^{(1)} = \varphi_k + \int G_0(\mathbf{r},\mathbf{r}')V_T(\mathbf{r}')\varphi_k(\mathbf{r}')d^3r', \tag{12}$$

which, used again on the right-hand side of Eq. (11) yields

$$\varphi_k^{(2)} = \varphi_k + \int G_0(\mathbf{r},\mathbf{r}')V_T(\mathbf{r}')\varphi_k(\mathbf{r}')d^3r' +$$
$$+ \int G_0(\mathbf{r},\mathbf{r}')V_T(\mathbf{r}')G_0(\mathbf{r}',\mathbf{r}'')V_T(\mathbf{r}'')\varphi_k(\mathbf{r}'')d^3r''d^3r' + \dots \tag{13}$$

and so on.

The power series thus obtained is the Born series. It is obvious that using $\psi_k^{(n-1)}$ in the following equation [10]

$$f = \frac{m}{2\pi\hbar^2} \int e^{-i\mathbf{k}_R\mathbf{r}'}V_T(\mathbf{r}')\psi_k d^3r, \tag{14}$$

which defines the scattering amplitude $f_k(\Omega)$, we obtain n-th order approximation for this quantity. In particular, the first Born approximation is

$$f_k(\theta) = \frac{m}{2\pi\hbar^2} \int e^{+i(\mathbf{k}-\mathbf{k}_R)\mathbf{r}}V_T(r)d^3r, \tag{15}$$

where θ stands for the scattering angle m for the electron mass and $\mathbf{k}_R$ denotes the wave vector of the diffracted electron in the place of detection ($|\mathbf{R}| \to \infty$).

An alternative approach consists of analysing the problem in separate partial wave components [10]. In the present paper, however, we do not discuss this approach, limiting ourselves to pointing out only that in this approach our temperature-dependent potential $V_V(\mathbf{r})$ can be very useful because it has the properties required for the partial wave analysis method.

In this paper we would like to concentrate our consideration on the scattering amplitude calculated by means of the first Born approximation for the temperature dependent potential $V_T(r)$. Introducing the scattering vector $\mathbf{k} = \mathbf{k'} - \mathbf{k}$ and taking into consideration the spherical symmetry properties of the scattering potential $V_T(\mathbf{r})$ we can write

$$f(\mathbf{K}) = \frac{Zem}{2\pi\hbar^2} \sum_{vj\kappa} \alpha_\kappa \langle n_{vj\kappa} \rangle e^{\frac{\beta_\kappa^2 B_{vj}}{2}} \int \frac{F_\kappa(|\mathbf{r} - \mathbf{R}_{vj}|)}{|r - R_{vj}|} e^{-i\mathbf{k}\mathbf{r}} d^3r =$$

$$= \frac{Ze^2 m}{2\pi\hbar^2} \sum_{vj\kappa} \alpha_k \langle n_{vj\kappa} \rangle e^{+\frac{\beta_\kappa^2 B_{vj}}{2} - i\mathbf{K}\mathbf{R}_{vj}^0} I_\kappa(\mathbf{K}), \tag{16}$$

where

$$I_\kappa(\mathbf{K}) = \int d^3r \frac{F_\kappa(|\mathbf{r}|)}{r} e^{-i\mathbf{k}\mathbf{r}}. \tag{17}$$

Using the explicit form of the integrand function F_κ (Eq. 17) the integral can be calculated and the result is

$$I_\kappa(\mathbf{K}) = \frac{4\pi}{K^2 + \beta_\kappa^2} e^{-\frac{K^2 B_{vj}}{2} - \frac{\beta_\kappa^2 B_{vj}}{2}}. \tag{18}$$

Then the scattering amplitude takes the form

$$f(\mathbf{K}) = \frac{2Ze^2 m}{\hbar^2} \sum_{vj\kappa} \left(\frac{\alpha_\kappa}{K^2 + \beta_\kappa^2} \right) \langle n_{v\mathbf{l}}^{\mathbf{j}} \rangle e^{-i\mathbf{K}\mathbf{R}_{vj}^0 - \frac{K^2 B_{vj}}{2}} \tag{19}$$

now taking into the mind the properties of the thin film we can use the equations

$$\langle n_{vj\kappa} \rangle = \langle n_{v\kappa} \rangle \tag{20}$$

and

$$B_{vj} = B_v, \tag{21}$$

which are the result of the fact that in the plane parallel to the surface the translation boundary conditions are fulfilled. Then we can write

$$f(\mathbf{K}) = F_{\|} \sum_{v-1}^{n} f_v(\mathbf{K}) e^{-W_v}, \tag{22}$$

where the quantities F, f_v, and W_v are defined as follows

$$F_{\|} = \sum_{\mathbf{j}} e^{-i\mathbf{K}_{\|}\mathbf{j}}, \tag{23}$$

$$f_v = \sum_{\kappa} \frac{2me^2 Z}{\hbar^2} \alpha_\kappa \frac{\langle n_{v\kappa} \rangle}{K^2 + \beta_\kappa^2} e^{-K_\perp va}, \tag{24}$$

$$W_v = \frac{1}{2} K^2 B_v = \frac{1}{2} \langle (\mathbf{K} \cdot \delta\mathbf{R}_{vj}^0)^2 \rangle, \tag{25}$$

where δR_{vj} denotes the displacement of the (vj)-th atom from its equilibrium position $(\delta R_{vj} = R_{vj} - R^0_{vj})$.

In the above equation a denotes the lattice constant, $aN = L$ is the normalization length in the plane parallel to the surface of the film, while $K_{||}$ and $K_{\perp}$ are the components of the scattering vector parallel and perpendicular to the surface plane of the film, respectively.

It is easy to see from Eq. (22) that the scattering amplitude of the film $f(K)$ is sum of the partial scattering amplitudes of the monoatomic layers f_v defined by Eq. (24). Each of the last amplitudes is multiplied by its own factor e^{-W_v} which we name the Debye—Waller factor, on the analogy of the bulk theory.

4. Electron density distribution in thin films

In the previous Section we have seen that our calculation of the LEED amplitude involves the determination of the electron density distribution across the thin film $\langle n_{vk} \rangle$. In this Section we consider this problem in detail. To describe a behaviour of the electrons in thin films, usually one supposes some boundary conditions for the wave functions on the surfaces. These boundary conditions depend on the nature of a concrete problem chosen to be considered. The boundary conditions for thin films have been discussed in the case of magnetic [2], superconducting [15], and semiconducting problems [16]. In these discussions thin films have been treated mainly in the effective mass approximation. There are other papers [1, 2, 5] where the boundary conditions are introduced in the natural way by means of the second quantization method. In this case a Hamiltonian describing the behaviour of the electrons in thin films has the general form [2]

$$H = \sum_{\lambda\mu} t_{\lambda\mu} a^t_{2\mu} a_{\mu\kappa} + \sum_{\lambda\mu\rho\kappa} \frac{1}{2} I_{\lambda\mu\rho\kappa} a^+_\lambda a^+_\mu a_\rho a_\kappa , \qquad (26)$$

where the indices λ, μ, ρ, κ represent the sets of the quantum numbers of the wave functions by means of which the matrix elements $t_{\lambda\mu}$ and $I_{\lambda\mu\rho\kappa}$ are calculated. By means of this Hamiltonian one can obtain any model used up to now in the theory of thin films [2]. Because of the complexity we expect, however, that the electron density distribution in thin films $\langle n_v \rangle$ can be in the first approximation sufficiently described by the following simplified form of Hamiltonian given by

$$H = \sum_{vjk} \sum_{v'j'\kappa'} t_{vjkv'j'\kappa'} c^+_{vjk} c_{v'j'\kappa'}. \qquad (27)$$

The form of the latter thin film Hamiltonian means that we suppose as the sets of the basic second quantization function the localized atomic orbitals of the free atom

$$|\lambda\rangle = |vj\kappa_{vj}\rangle = |vj\kappa\rangle , \qquad (28)$$

where νj determine the position of the atom in thin film and $\kappa_{\nu j}$ its orbital quantum numbers of the free atom. The Hamiltonian (27) has been used many times in the theory of thin films [2]. We use it here, however, in its temperature-dependent form modified by the crystal potential $V_T(r)$. In this case the matrix elements $t_{\nu j \kappa \nu' j' \kappa}$ are changed by $t^T_{\nu j \kappa \nu' j' \kappa}$ and we define them as follows. The diagonal elements $t^T_{\nu j \kappa \nu j \kappa}$ are of the form

$$t^T_{\nu j \kappa \nu j \kappa} = E_\kappa + A^T_\kappa(\nu), \tag{29}$$

where

$$A^T_\kappa(\nu) = \langle \nu j \kappa | (V_T^{(r)} - V_0(\mathbf{r} - \mathbf{R}_{\nu j})) | \nu j \kappa \rangle, \tag{30}$$

but nondiagonal elements are given by

$$t^T_{\nu j \kappa \nu' j' \kappa} = - B^T_\kappa(\nu \nu') \qquad \kappa = \kappa' \tag{31}$$

and

$$B^T_\kappa(\nu \nu') = \langle \nu j \kappa | \{ V_T(r) - V_0(\mathbf{r} - \mathbf{R}_{\nu' j'}) \} | \nu' j' \kappa \rangle. \tag{32}$$

In this model we are dealing with the matrix elements for the difference between the temperature-dependent crystal potential $V_T(r)$ and the static atom potential $V_0(\mathbf{r} - \mathbf{R}_{\nu j})$ localized at the νj-th site of the thin film lattice calculated by means of the two atomic orbitals of the free atom localized in the same site νj (30) and by means of the two atomic orbitals localized in the different site (32) of the crystal lattice. The other quantity which appears in Eq. (29) i.e. free atomic orbitals energy E^0_κ are the eigenvalues of the equation

$$\left[\frac{\rho^2}{2m} + V_0(\mathbf{r} - \mathbf{R}_{\nu j}) \right] | \nu j \kappa \rangle = E^0_\kappa | \nu j^\kappa \rangle. \tag{33}$$

Now we can use the Green function method to calculate the electron density distribution in thin films the Hamiltonian of which is

$$H = \sum_{\nu j \kappa \nu' j' \kappa'} t^T_{\nu j \kappa \nu' j' \kappa'} c^+_{\nu j \kappa} c_{\nu' j' \kappa'}. \tag{34}$$

The procedure is known from the the static potential case [2]. Defining as usual the following set of Green functions

$$G_{\nu j \kappa \nu' j' \kappa'} = \langle\langle c_{\nu j \kappa} | c^+_{\nu' j' \kappa'} \rangle\rangle \tag{35}$$

and setting for them the equations of motion one has to solve the following sets of the equations

$$E G_{\nu j \kappa \nu' j' \kappa'} = \delta_{\nu j \kappa \nu' j' \kappa'} + \sum_{\nu'' j'' \kappa''} t^T_{\nu j \kappa \nu'' j'' \kappa''} G_{\nu'' j'' \kappa'' \nu' j' \kappa'}. \tag{36}$$

The method of the solution of these equations is given in [2] for the Hamiltonian (27) and we do not repeat it here. The only difference for our temperature-dependent Hamiltonian (34) is that the matrix elements are now temperature-dependent. Using then the method presented in [2] for the sought solution of Eq. (36) one obtains the following Green functions for the present problem

$$G_{\nu j \kappa \nu' j' \kappa'} = \sum_{\tau \mathbf{h}} \Gamma^{\mathbf{h} \kappa}_{\nu \tau} \Gamma^{\mathbf{h} \kappa}_{\nu' \tau} e^{i \mathbf{h}(j' - j)} \frac{\delta_{\kappa \kappa'}}{E - E_{\tau \mathbf{h}}}, \tag{37}$$

where coefficients $\Gamma_{v\tau}^{h\kappa}$ are the solutions of the following sets of equations

$$\sum_{\bar{v}\,\bar{\kappa}} (t_{v\kappa\bar{v}\bar{\kappa}}^{T}\Gamma_{\bar{v}\tau}^{h\bar{\kappa}} - E_{\tau h\kappa}\delta_{\bar{v}v}\delta_{\bar{\kappa}\kappa}\Gamma_{\bar{v}\tau}^{h\bar{\kappa}}) = 0, \tag{38}$$

where $E_{\tau h\kappa}$ are given by

$$\sum_{\bar{v}\,\bar{\kappa}} t_{v\kappa\bar{v}\bar{\kappa}}^{T}\Gamma_{\bar{v}\tau}^{h\bar{\kappa}}G_{\tau h}^{\bar{\kappa}\kappa'} = E_{\tau h\kappa}\Gamma_{v\tau}^{h\kappa}G_{\tau h}^{\kappa\kappa'}, \tag{39}$$

$$t_{v\kappa\bar{v}\bar{\kappa}}^{T} = \sum_{d} t_{vj\bar{v}\bar{j}\bar{v}}e^{ih(j-\bar{j})}, \tag{40}$$

and can be generally written in the form [1]:

$$\Gamma_{v\tau}^{h\kappa} = A_{\tau}^{h\kappa}\cos(\alpha_{\tau}^{T}v + \beta_{\tau}^{T}). \tag{41}$$

About the coefficients $\Gamma_{v\tau}^{h\kappa}$ from now we suppose that they do not depend on the quantum number κ, i.e. we put

$$\Gamma_{v\tau}^{h\kappa} = \Gamma_{v\tau}^{h} = A_{\tau}^{h}\cos(\alpha_{\tau}^{T\,v} + \beta_{\tau}^{T}), \tag{42}$$

where A_{τ}^{h} is the normalization constant and coefficients α_{τ}^{T} and β_{τ}^{T} are the temperature-dependent quantity which can be calculated numerically only. We suppose, however, that they can be used in the same analytical form as in the static potential case. The other relations between α_{τ}^{T} and β_{τ}^{T} are dependent on the crystallographic structure and the orientation of the sample and are the same as between α_{τ} and β_{τ} (see [1]).

By means of the Green function $G_{vj\kappa\,v'j'\kappa'}$ thus determined we can simply express the electron density distribution across the thin film, namely, we have

$$\langle n_{v\kappa}\rangle \equiv \langle n_{vj\kappa}\rangle = \langle c_{vj\kappa}^{t}c_{vj\kappa}\rangle =$$

$$= \frac{i}{2\pi}\lim_{\varepsilon\to 0}\int_{-\infty'}^{\infty'} dE \sum_{\tau h\kappa} \frac{G_{\tau h\kappa}(E+i\varepsilon) - G_{\tau h\kappa}(E-i\varepsilon)}{e^{\frac{E-E_{F}^{\ddag}}{kT}}+1}(\Gamma_{v\tau}^{h})^{2} = \sum_{\tau h\kappa}(\Gamma_{v\tau}^{h})^{2}f(E_{\tau h\kappa}), \tag{43}$$

where $f(E_{\tau h\kappa})$ is the Fermi distribution function

$$f(E_{\tau h\kappa}) = \frac{1}{e^{\frac{E_{\tau h v} - E_{F}}{k_{B}T}}+1}. \tag{44}$$

There $E_{\tau h\kappa'}$ denote the energy of the electrons in the thin film and E_{F} stands for the temperature-dependent Fermi energy of thin film, in κ-th band. The energy of the electron in thin crystal films is actually given approximately by the following expression

$$E_{\tau h\kappa} = E_{\kappa}^{0} + A_{\kappa}^{T} \pm 2B_{\kappa}^{T}(\cos h_{x}a + \cos h_{y}a + \cos \alpha_{\tau}a). \tag{45}$$

This equation describes the temperature-dependence of the band structure of thin films. This temperature-dependence of the band structure corresponds to the low energy electron diffraction spectra calculated in the dynamical theory of LEED.

Using Eq. (45) one can calculate the Fermi energy for each band which is created by the given free atomic orbitals κ. Now we limit our consideration to the one band approximation, i.e. we suppose that all free atomical orbitals κ in thin films are sufficiently localized in the energy space except the valence orbital which creates the film conduction subbands numbered by index τ. In this simple case the electron density distribution can be written by

$$\langle n_{v\kappa}\rangle = \begin{cases} \mu \\ \langle n_{vw}\rangle \end{cases},\tag{46}$$

where μ denotes the number of electrons for κ-th orbital if it is not a valence orbital (κ includes the degeneracy of the orbital due to the spin σ). For the valence orbital we then have $\langle n_{vw}\rangle$, which we can write as

$$\sum_{\tau}\frac{S}{4\pi^2}(T_{v\tau}^{h})^2\int f(E_{\tau h}^T)d^2h = \langle n_v\rangle.\tag{47}$$

The Fermi energy for the valence band can be calculated by means of the normalization condition of the Fermi distribution

$$2\sum_{\tau h}f(E_{\tau h})=nN^2,\tag{48}$$

where factor 2 stands for the spin degeneration of the electrons, nN^2 denotes the number of the valence electrons in the thin film, and the energy

$$E_{\tau h}=\frac{\hbar^2 h^2}{2m}+\varepsilon_0\tau^2\qquad (\tau=1,2,\ldots)\tag{50}$$

is counted from the low energy edge of the valence band.

The normalization condition (48) leads to the equations

$$kT\sum_{\tau=1}^{M}\ln\left[\frac{1}{2}(1+e^{\frac{E-\varepsilon_0\tau^2}{kT}})\right]-\frac{\pi n h^2}{ma^2}0\tag{51}$$

$$M=\text{Integer}\left(E:\varepsilon_0\right)^{1/2}\tag{52}$$

which must be solved numerically for energy E. Then for the effective number distribution of the valence electrons in the direction perpendicular to the surface of the film we obtain

$$\langle m_{vw}\rangle = \frac{2mkTa^2}{\pi\hbar^2}\frac{1}{n}\sum_{\tau=1}^{M}\frac{2\cos^2(\alpha_\tau^T v+\beta_\tau^T)}{\left(n+\dfrac{\sin(\alpha_\tau^T n)\cos[\alpha_\tau^T(n+1)+2\beta_\tau^T]}{\sin\alpha_\tau^T}\right)}\ln\left[\frac{1}{2}(1+e^{\frac{E_F-\varepsilon_0\tau^2}{kT}})\right]\tag{53}$$

$$M=\text{Integer}\left(\frac{E_F}{\varepsilon_0}\right)^{1/2}\tag{54}$$

Equations (51) with (53) and (54) determine the electron density distribution in thin films in the case of the one band approximation.

5. Distribution of the Debye—Waller factors for thin films in pseudoharmonic approximation

The calculation of the scattering amplitude for the LEED experiments interpretation by means of our formula (22) involves not only the determination of the electron density distribution in thin films, which we considered in the previous Section, but it also involves the calculation of the distribution of the Debye- Waller factors in thin films. This calculation can be done by means of a method presented in our previous paper [9] where we have discussed the Debye—Waller factors for thin films in harmonic and pseudoharmonic approximation, and for that reason in this Section we give only the essential relations and definitions which are necessary for future numerical calculations.

At first the Debye—Waller factor g_v for a given monoatomic layer v is defined by the equation

$$g_v = e^{-W_v},$$
(55)

where the Debye—Waller coefficient W_v is given by

$$W_v = \frac{1}{2} \langle (\mathbf{K} \cdot \delta \mathbf{R}_{vj})^2 \rangle$$
(56)

and $\mathbf{K}$ denotes the scattering vector $\mathbf{K} = \mathbf{K}' - \mathbf{K}$, while $\delta \mathbf{R}_{vj}$ denotes as usual the displacement vector of the vj-th atom.

The phonons theory elaborated by Wojtczak and Zajac [1] allows to express the displacement $\delta \mathbf{R}_{vj}$ by means of creation $a^t_{\mathbf{q}\lambda\mu}$ and annihilation operators $a_{\mathbf{q}\lambda\mu}$ and phonons amplitudes $T^{\mathbf{q}}_{v\lambda}$ as follows

$$\delta \mathbf{R}_{vj} = \left(\frac{\hbar}{2MN^2 n} \right)^{1/2} \sum_{\mathbf{q}\lambda\mu} \frac{e_{\mathbf{q}\lambda\mu}}{\sqrt{\omega_{\mathbf{q}\lambda\mu}}} T^{\mathbf{q}}_{v\lambda} e^{i\mathbf{q}j} (a_{\mathbf{q}\lambda\mu} + a^t_{\mathbf{q}\lambda\mu}).$$
(57)

$\omega_{\mathbf{q}\lambda\mu}$ are the frequency eigenvalues of phonons, N^2 denotes the number of atoms in each atomic layer, n denotes the number of the atomic layers parallel to the surfaces of the film while $e_{\mathbf{q}\lambda\mu}$ denotes the polarization vector of the phonon in $(\mathbf{q}\lambda\mu)$ state. By means of Eq. (57) the Debye—Waller coefficient W_v (Eq. 56) can be expressed as

$$W_v = \frac{\hbar K^2}{4MN^2 n} \sum_{q\lambda} T^2_{v\lambda} \left\{ \sin^2 \theta \cos^2 \varphi \frac{\text{cth} \left(\frac{\hbar\omega_{\mathbf{q}\lambda 1}}{2KT} \right)}{\omega_{\mathbf{q}\lambda 1}} + \right.$$

$$\left. + \sin^2 \theta \sin^2 \varphi \frac{\text{cth} \left(\frac{\hbar\omega_{\mathbf{q}\lambda 2}}{2KT} \right)}{\omega_{\mathbf{q}\lambda 2}} + \cos^2 \theta \frac{\text{cth} \left(\frac{\hbar\omega_{\mathbf{q}\lambda 3}}{2KT} \right)}{\omega_{\mathbf{q}\lambda 3}} \right\} \Lambda$$
(58)

where the frequencies $\omega_{\mathbf{q}\lambda 1} = \omega_{\mathbf{q}\lambda 2}$ and $\omega_{\mathbf{q}\lambda 3}$ in the pseudoharmonic case are given by

$$\omega_{\mathbf{q}\lambda 1} = \alpha_T \omega^0_{\mathbf{q}\lambda 1},$$
(59)

$$\omega_{\mathbf{q}\lambda 3} = \alpha_T \omega^0_{\mathbf{q}\lambda 3}$$
(60)

and $\omega^0_{q\lambda\mu}$ denote the harmonic frequency and we approximate them by

$$\omega^0_{q\lambda 1} = \omega_m \sqrt{\sin^2 \frac{q_x a}{2} + \sin^2 \frac{q_y a}{2} + \frac{A'}{A} \sin^2 \frac{\alpha_\lambda}{2}}, \tag{61}$$

$$\omega^0_{q\lambda 3} = \bar{\omega}_m \sqrt{\sin^2 \frac{q_x a}{2} + \sin^2 \frac{q_y a}{2} + \frac{B'}{B} \sin^2 \frac{\alpha_\lambda}{2}}, \tag{62}$$

$$\omega_m = \sqrt{\frac{4A}{M}}; \qquad \bar{\omega}_m = \sqrt{\frac{4B}{M}}, \tag{63}$$

where A, A' and B, B' denote the force constants by means of which we describe the interaction between two atoms inside the film and on the surface. The renormalization coefficient α_T which is temperature-dependent and is defined by the rate of the pseudoharmonic and harmonic force contstants, can be calculated by means of the Siklós method [4, 5, 9, 8]. Supposing that it is the same for all branches μ one obtains

$$\alpha_T^2 = 1 - \frac{36}{a^2} \left[\frac{1}{2n} \sum_{\nu=1}^n \langle (\delta R_{\nu j} - \delta R_{\nu+1 j})^2 + (\delta R_{\nu j} - \delta R_{\nu-1 j})^2 \rangle \right]. \tag{64}$$

The sum over q, due to the periodic conditions which are fulfilled in the direction parallel to the plane of the film, can be replaced by an integral using the relation

$$\sum_q (\ldots) = \frac{S}{4\pi} \int_{-\frac{\Pi}{a}}^{\frac{\Pi}{a}} \int_{\frac{\Pi}{a}}^{\frac{\Pi}{a}} dq_x dq_y (\ldots), \tag{65}$$

thus Eq. (58) becomes

$$W_\nu = \frac{\hbar K^2 kT}{4MN^2 m} \sum_{\lambda=1} \{ I_1(\lambda) \sin^2 \theta + I_3(\lambda) \cos^2 \theta \}, \tag{66}$$

where

$$I_1(\lambda) = \frac{4N^2 kT}{\pi \hbar \omega_m^2 \alpha_T^2} \ln \frac{\mathrm{sh}\left(\frac{\hbar \omega_m \alpha_T}{2kT} \sqrt{2 + \varepsilon_A \sin^2 \frac{\alpha_\lambda}{2}} \right)}{\mathrm{sh}\left(\frac{\hbar \omega_m \alpha_T}{2kT} \sqrt{\varepsilon_A \sin^2 \frac{\alpha_\lambda}{2}} \right)}, \tag{67}$$

$$I_3(\lambda) = \frac{4N^2 kT}{\pi \hbar \bar{\omega}_m^2 \alpha_T^2} \ln \frac{\mathrm{sh}\left(\frac{\hbar \bar{\omega}_m \alpha_T}{2kT} \sqrt{2 + \varepsilon_B \sin \frac{2\alpha_\lambda}{2}} \right)}{\mathrm{sh}\left(\frac{\hbar \bar{\omega}_m \alpha_T}{2kT} \sqrt{\varepsilon_B \sin^2 \frac{\alpha_\lambda}{2}} \right)}, \tag{68}$$

$$\varepsilon_A \equiv \frac{A'}{A}; \qquad \varepsilon_B \equiv \frac{B'}{B} \tag{69}$$

and we have made the use of the fact that in our model $\omega_{j\lambda 1} = \omega_{q_{\lambda 2}}$. Introducing the following quantity

$$
\eta_v(n) = \frac{1}{n} \sum_{\lambda=1}^{n} T_{v\lambda}^2 \ln \frac{\text{sh} \left(\frac{\hbar \omega_m \alpha_T}{2kT} \sqrt{2 + \varepsilon_A \sin^2 \frac{\alpha_\lambda}{2}} \right)}{\text{sh} \left(\frac{\hbar \omega_m \alpha_T}{2kT} \sqrt{\varepsilon_A \sin^2 \frac{\alpha_\lambda}{2}} \right)} \quad , \tag{70}
$$

$$
\gamma_v(n) = \frac{1}{n} \sum_{\lambda=1}^{n} T_{v\lambda}^2 \ln \frac{\text{sh} \left(\frac{\hbar \bar{\omega}_m \alpha_T}{2kT} \sqrt{2 + \varepsilon_B \sin^2 \frac{\alpha_\lambda}{2}} \right)}{\text{sh} \left(\frac{\hbar \bar{\omega}_m \alpha_T}{2kT} \sqrt{\varepsilon_B \sin^2 \frac{\alpha_\lambda}{2}} \right)} \quad , \tag{71}
$$

then we can rewrite Eq. (66) in the form

$$
W_v = \frac{K^2 kT \eta_v(n)}{\pi M \omega_m^2 \alpha_T^2} \left[\sin^2 \theta + \frac{\omega_m^2}{\bar{\omega}_m^2} \frac{\gamma_v(n)}{\eta_n(n)} \cos^2 \theta \right] =
$$

$$
= \frac{K^2 kT \eta_v(n)}{4\pi A \alpha_T^2} [1 + \xi_n(n) \cos^2 \theta] , \tag{72}
$$

where

$$
\xi_v(n) = \frac{\omega_m^2}{\bar{\omega}_m^2} \frac{\gamma_v(n)}{\eta_v(n)} - 1 = \frac{A}{B} \frac{\gamma_v(n)}{\eta_v(n)} - 1 \tag{73}
$$

and be called the anisotropy coefficients of the Debye—Waller factor for the v-th monoatomic layer of the film.

From the last form for the W_v-coefficient one can see the anisotropic character of the Debye—Waller factor as well as its position and the thickness-dependence.

6. Conclusion

In this paper we have presented the theoretical model of the description of the low energy electron diffraction by thin films using the field theory methods known in the literature. In the paper the expression of the scattering amplitude for the electron scattered by the film into the component amplitudes of the given monoatomic layers is a natural consequence of introducing the dynamical scattering potential which depends on temperature as well as on the position of the scattering atoms in the thin film. Using the field theory method allowed us to calculate the approximate electron distribution across the film as well as the distribution of the Debye—Waller factor of thin film, which are involved in the calculation of the component amplitudes of the electron scattered by the particular monoatomic layers.

Due to the pseudoharmonic approximation by means of which in our model the lattice dynamics of thin film atoms is treated, one can use this model to search for the

low energy electron diffraction problem in the harmonic as well as in the anharmonic case of thin films. In particular, it can be useful to study the effect of the change of the surface lattice constants, which, as is known from LEED experiments, changes the location of the suitable Bragg's peaks on the energetic scale.

Concluding we would like to point out that the theoretical approach to the LEED problem presented here is sufficiently complete to be treated numerically. We have done such a numerical investigation and present the results in a supplementary paper [17].

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