Determination of Debye–Waller factors from elastic diffraction peaks of thermal energy atomic scattering from solid surfaces

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An efficient inverse procedure to solve the inverse scattering problem has been developed and the Debye–Waller factors have been determined from the elastic diffraction peaks of only one experimental setup (one data set) of thermal energy atomic scattering from solid scattering from solid surfaces. The new inverse procedure preserves the correlation between elastic scattering and thermal attenuation. The computations of the sophisticated He scattering from LiF(001) surface support the correctness of the new procedure. The computations have been compared with the results of the analysis of several different experimental setups. © 1998 Elsevier Science Ltd. All rights reserved

1. Introduction

In the case of thermal energy atomic scattering from solid surfaces (TEAS), the neutral probe particles (usually He atoms) have approximately 20 to 100 meV energy. This corresponds to the thermal energy. TEAS is particularly sensitive to the topmost layer of the solid surfaces.[1] The probe particles do not penetrate into the surface and their classical turning point is about 0.3 to 0.4 nm from the surface. These properties give a golden opportunity to investigate the surface structure, the dynamics of the inelastic processes, and surface impurities. For example, TEAS is sensitive for an adsorbed layer on the surface, is a non-destructive method and is not disturbed by the deeper layers. The surface dynamics can be explored by the time-of-flight measurement of the probe particles (inelastic scattering: phonon creation and annihilation). Individual surface impurities have a large cross-section for the diffuse scattering, so the presence of these impurities on a surface has a measurable effect. If we want to analyze the surface structure by diffractive scattering, thermal attenuation has relevant influence on the intensities of the scattering peaks. Diffractive scattering cannot be described without considering thermal attenuation. Our goal is to introduce an appropriate model and an inverse procedure to resolve this problem.

2. Scattering model

If we choose a time independent interaction potential to describe the thermal energy atomic scattering from solid, supposing perfect surfaces which are realized well nowadays, the calculated diffraction peaks have much higher values than those obtained from the experiments. This leads to hard difficulties. On the other hand, this phenomenon hides the possibility of this method to examine the dynamics of the processes on the surfaces. The chosen time independent model of the atomic scattering from a periodic surface is able to reproduce the elastic diffractive scattering and the bound state resonance, but unable to render an account of the elastic non-diffractive scattering, the inelastic scattering, the physisorption, and the chemisorption. If we want to investigate only the structure of surfaces and not the catalysis on a surface, we only have to consider the elastic diffractive and non-diffractive scattering, the bound state resonance and the inelastic scattering. The application of the Debye–Waller factor is a common method to consider the thermal attenuation of the diffraction peaks. The Debye–Waller factor is appropriate to describe the elastic non-diffractive scattering and the inelastic scattering (phonon creation and phonon annihilation) according to its kinematic and dynamic theory. Merging the time-independent model of TEAS and the theory of the Debye–Waller factor we get an efficient model to investigate the surface structure. In this paper we try to compose this idea into the language of mathematics. In the case of TEAS special considerations have to be taken to model the Debye–Waller factors. The traditional kinematic theory of the Debye–Waller factor is a good starting-point because—based on experiments—the temperature increase of the solid surface leads to an approximately exponential decrease of the diffraction peaks. First of all, we have to give the definition of the Debye–Waller factor (DWf) so that it can be handled in a correct way. This is a factor that provides relationship between I^v and I^f intensities in every diffraction direction, where the "v" and "f" superscripts mean the thermally vibrating and the frozen crystal, respectively. Thus, $DWf = I^v/I^f$. Taking into consideration everything strictly, the DWf of a given experimental setup is different in every open channel.

The effect of the crystal vibration was investigated first by Debye and Waller.[2] A short summary of this topic can be found in.[3] This theory has been developed in several fields of physics, e.g. in the case of electron diffraction,[4] neutron diffraction[5] and TEAS.[6,7] Beside the theoretical approach, the experimental results have to be considered to fit the unknown model parameters. Bortolani and his coworkers[8] have carried out detailed experiments to determine the behavior of *DWf* of He–Pt(111) scattering that has poor diffraction pattern since only one diffraction peak—the specular peak—exists. Otherwise, generally several different experimental setups are used to fit the *DWf*. In this paper a new method is presented to determine the *DWf*s based on the results of one single experimental setup, which furnishes rich diffraction patterns, e.g. He scattering from clean ionic surfaces or from adsorbed layers of metal surfaces.

3. Inverse procedure

Practically, our method is a sort of the inverse procedures. The inverse procedure determines the unknown parameters of the scattering model from the intensity distribution in general. We fit the parameters of the time independent model and of the Debye–Waller factors to the measured intensities at the same time contrary to the traditional methods.[9–15] The traditional methods of the inverse scattering reduce the problem to fit the parameters of the frozen surface and do not handle the effect of vibrations. The Debye–Waller factors is neglected or gained from several experimental arrangements by interpolation. We do not separate these parameters into two independent groups, so we manage to preserve the correlation between the elastic diffraction peaks and the thermal attenuation. This is the central idea of the present paper. The advantage of this procedure is that only one experimental setup is needed. The disadvantage is that more parameters have to be fitted.

Generally, the mathematical formulation is to minimize the following expression:

$$D(\mathbf{V}) = \sqrt{\sum_{\{\mathbf{G}\}} (I_{\mathbf{G}}^{\mathrm{f}}(\{h_i\}) \cdot DWf_{\mathbf{G}}(\{p_i\}) - I_{\mathbf{G}}^{\mathrm{v}})^2}, \tag{1}$$

where $\mathbf{V} = \{h_i\} \bigcup \{p_i\}$, $\{h_i\}$ is the set of the unknown parameters of the chosen time independent model to describe the scattering, $\{p_i\}$ is the set of the unknown parameters of the Debye–Waller factors, and $\{\mathbf{G}\}$ describes all the open channels. Function D measures the distance between the experimental and the model calculated intensities choosing Euclidean norm, which may have many unknown parameters. Therefore, *DWf*s are also described by their unknown model parameters. Reasonable physical constraints make the model more robust. Suitable constraints may regard the average *DWf* in the following way:

$$\sum_{\{\mathbf{G}\}} I_{\mathbf{G}}^{\mathrm{f}} \cdot DWf_{\mathbf{G}} - \sum_{\{\mathbf{G}\}} I_{\mathbf{G}}^{\mathrm{v}} = 0, \tag{2}$$

where $\{\mathbf{G}\}$ means all the open channels and

$$I_{\mathbf{G}}^{\mathrm{f}} \cdot DWf_{\mathbf{G}} - I_{\mathbf{G}}^{\mathrm{v}} = 0 \tag{3}$$

holds for the few most dominant intensities. This ensures the deciding role of the largest intensities of the diffraction pattern.

The eqns (1) to (3) represent the model in general. These are useful for every time independent model. However, the details of every model are different.

4. Results and discussion

Now we show an important application using the Hard Corrugated Wall model (HCW).[15–22] According to HCW model the scattered particle does not feel interaction during the approach of the surface, but the particle collides suddenly into an infinite potential wall. This potential wall describes the surface by its corrugation. The investigated application is the thermal energy He scattering from LiF(001) surface.[23] We have chosen this experimental setup because it is published in detail sufficiently and there are computational results of the traditional inverse procedure[15] too. He–Lif(001) scattering is a complicated system of the thermal energy atom scattering because of the great number of diffraction peaks. Therefore, the calculation of the Debye–Waller factors and of the corrugation parameters (these are the unknown parameters of the time independent model, e.g. the HCW model) is not a trivial procedure. Consequently, this scattering problem is appropriate to decide whether the new method is efficient or not. From our point of view the role of the HCW model is basic to determine the initial values of the unknown parameters of more sophisticated models in connection with TEAS since HCW model is able to describe the TEAS in the first approach without applying unreasonably long computing time. As is known, for finding the minimum the initial values are always of crucial importance.

For example, the HCW model can be solved by the GR method. A brief description of the GR method is the following:[15,18,19,21,22] The infinite hard wall is depicted by the function $z = z_1(\mathbf{R})$, where the vector $\mathbf{R} = (x, y)$ is parallel to the surface. It means that the interaction potential is zero above the surface and infinite below the surface. For a square unit cell the corrugation function can be given by the first two terms if its Fourier series:

$$z_1 = h_1 \left[\cos\frac{2\pi}{a}x + \cos\frac{2\pi}{a}y \right] + h_2 \cos\frac{2\pi}{a}x \cos\frac{2\pi}{a}y, \tag{4}$$

where h_1 and h_2 are corrugation parameters, and "a" is the lattice constant. For the incident wave vector $\mathbf{k}_i$ and for each two-dimensional reciprocal lattice vector $\mathbf{G}$ the energy conservation in the case of elastic scattering requires that

$$k_{\mathbf{G}z}^2 = k_i^2 - (\mathbf{K}_i + \mathbf{G})^2, \tag{5}$$

where $\mathbf{K}_i$ is the component of the incident wave vector parallel to the surface. As is well known, there is a finite number of $\mathbf{G}$ vectors (called $\mathbf{F}$ vectors, for which $k_{\mathbf{F}z}^2 > 0$) representing the diffracted outgoing beams. The intensities $I_{\mathbf{F}}$ of the $\mathbf{F}$ beams satisfy the sum rule:

$$\sum_{\mathbf{F}} I_{\mathbf{F}} = 1, \quad I_{\mathbf{F}} = \frac{k_{\mathbf{F}z}}{k_z} |A_{\mathbf{F}}|^2, \tag{6}$$

k_z being the value $k_{\mathbf{F}z}$ when $\mathbf{F} = 0$ (specular beam). When $x \Leftarrow z_1(\mathbf{R})$, the potential energy will be infinite and the wave function must be equal to zero. ($\mathbf{r} = (\mathbf{R}, z)$ is the position vector, z being the direction perpendicular to the surface.) The consequence of this condition is the system of equations

$$\psi[\mathbf{R}, z_1(\mathbf{R})] = 0, \tag{7}$$

$$\sum_{\{\mathbf{G}\}} \exp\{i[(k_{\mathbf{G}z} + k_z)z_1(\mathbf{R}) + \mathbf{G}\mathbf{R}]\} A_{\mathbf{G}} = -1, \tag{8}$$

if the total wave function is approximated by virtue of Rayleigh ansatz :[24]

$$\psi[\mathbf{R}, z) = \sum_{\{\mathbf{G}\}} \{\delta_{\mathbf{G},0} \exp[-ik_{\mathbf{G}z}z] + A_{\mathbf{G}} \exp[ik_{\mathbf{G}z}z]\} \quad (9)$$

$$\times \exp[i(\mathbf{K}_i + \mathbf{G})\mathbf{R}].$$

The first term represents the incident beam and the others the diffracted beams corresponding to each two-dimensional reciprocal lattice vector $\mathbf{G}$, with propagation vectors $\mathbf{k}_{\mathbf{G}}(\mathbf{K}_i + \mathbf{G}, k_{\mathbf{G}z})$. The amplitudes $A_{\mathbf{G}}$ must satisfy eqn (8) for all the points $\mathbf{R}$ of the crystal surface and for all vectors $\mathbf{G}$. In GR method the amplitudes $A_{\mathbf{G}}$ are to be calculated depending on the points chosen in the space $\mathbf{G}$ and in the unit cell of $\mathbf{R}$, respectively. For the calculation of N complex amplitudes $A_{\mathbf{G}}$ the eqn (8) provides the necessary $2N$ real or N complex equations.

Moreover, we have derived a possible kinematic expression of the DWf from eqn (10):

$$\exp(-2W_{\mathbf{G}}) = DWf_{\mathbf{G}} = I_{\mathbf{G}}^v / I_{\mathbf{G}}^f, \quad (10)$$

namely:

$$W_{\mathbf{G}} = \frac{\ln(I_{\mathbf{G}}^v / I_{\mathbf{G}}^f)}{-2}. \quad (11)$$

This leads to an efficient, partly explicit construction of the inverse procedure. To investigate this expression in detail let us consider the following formula of Debye–Waller factor:

$$DWf = \exp(-2W), \quad W = \tfrac{1}{2}\langle(\Delta\mathbf{k} \cdot \mathbf{u})^2\rangle, \quad (12)$$

where $\Delta\mathbf{k}$ is the change of wave vector of the scattering beam, $\mathbf{u}$ is the displacement vector taken from the equilibrium point of surface atom, and $\langle\rangle$ denotes the thermal average.[7]

For simplicity, we assume an incident angle of He beam $\Theta_i = 0°$. Then for every open channel:

$$\Delta k_{\mathbf{G}} = \Delta k_{\mathbf{O}} \cdot \cos(\Theta_f/2), \quad \Delta k_{\mathbf{O}} = 2 \cdot |k_i|, \quad (13)$$

where the subscript i means the state before the scattering and subscript f that after the scattering. Moreover, if the axes x and y parallel and axis z perpendicular to the surface have angles α, β and γ of inclination to the vector $\Delta k_{\mathbf{G}}$, then

$$W_{\mathbf{G}} = \tfrac{1}{2}(\Delta k_{\mathbf{G}})^2 \langle[(u_x, u_y, u_z) \cdot (\cos\alpha, \cos\beta, \cos\gamma)]^2\rangle. \quad (14)$$

In the first approach we may say that $\langle u_x \cdot u_y \rangle$, $\langle u_x \cdot u_z \rangle$, $\langle u_y \cdot u_z \rangle$ are equal to zero and for He–LiF(001) scattering $\langle u_x^2 \rangle = \langle u_y^2 \rangle$ because of the symmetry. Considering eqn (13) we get:

$$W_{\mathbf{G}} = 2 \cdot |k_i|^2 \cdot \cos^2(\Theta_f/2) \quad (15)$$

$$\times [\langle u_x^2 \rangle(\cos^2\alpha + \cos^2\beta) + \langle u_z^2 \rangle \cos^2\gamma],$$

where Θ_f points to the direction of the open channel $\mathbf{G}$ after the scattering. Since $\Delta\mathbf{k}_{\mathbf{G}} = \mathbf{k}_{\mathbf{G}} - \mathbf{k}_i$, $\mathbf{k}_{\mathbf{G}} = (G_x, G_y, |k_i|\cos(\Theta_f))$ and $\mathbf{k}_i = (0, 0, -|k_i|)$, so $\cos\alpha = G_x/\Delta k_{\mathbf{G}}$, $\cos\beta = G_y/\Delta k_{\mathbf{G}}$ and $\cos\gamma = (|k_i| + |k_i|\cos\Theta_f)/\Delta k_{\mathbf{G}} = \cos(\Theta_f/2)$.

Above we described a kinematic approach of DWf which gives different values in the corresponding directions of open channels. In this example not only the amplitudes of the corrugation function but also the parameters $\langle u_x^2 \rangle$ and $\langle u_z^2 \rangle$ have to be fitted to the experimental results.

Let us take into account eqn (15) which provides a special

expression of DWf after all. This expression is suitable to realize the inverse procedure, because the parameters $\langle u_x^2 \rangle$ and $\langle u_z^2 \rangle$ can be evaluated explicitly using the intensities of the atoms scattered from the frozen and from the vibrating surface using eqns (10) and (11). Otherwise, eqns (10) and (11) correspond to eqn (3). We may receive an over-determined system of the linear equations prescribing eqn (11) for the most dominant intensities. It can be solved by the physically reasonable nonnegative least square method.[25] It means such a solution of the over-determined system of the linear equations that is contented by the vector of the solution having only greater than or equal to zero elements in the sense of the least squares.

Then the process to determine the optimal parameters is the following. First of all we calculated the intensities $I_{\mathbf{G}}^f$ for fixed corrugation amplitudes by the GR method and using few most dominant intensities we determine the values of $\langle u_x^2 \rangle$ and $\langle u_z^2 \rangle$ by eqn (11). By means of these values we can compute the corresponding Debye–Waller factors in every open channel, so we can compute the norm $D(\mathbf{V})$, also defined by eqn (1). In this way we get the optimum corrugation parameters according to the minimum of the norm $D(\mathbf{V})$. Thus, for the determination of the optimum corrugation parameters an implicit method, e.g. the gradient method has to be used.

The advantage of the above mentioned method is that we can get the optimum parameters more safely, because we have to fit only two parameters implicitly and not four. The most important data of the experiment are the following:[23] the surface temperature is 80 K, the wave number of the incident He atom is $\langle k_i \rangle = 109.5$ nm^{-1}, the incident angle of the He beam is $\Theta_i = 0°$, the lattice constant of the LiF(001) clean surface is $a = 0.284$ nm, the average DWf is 0.283, the number of the open channels is 69 and the five most dominant intensities are $I_{(2,2)}^v = 0.0207$, $I_{(2,0)}^v = 0.0108$, $I_{(2,1)}^v = 0.0068$, $I_{(2,3)}^v = 0.0054$, and $I_{(1,0)}^v = 0.0035$. These five open channels mean 28 open channels with their symmetric partners. The regions of the searching are 0.01 nm $< h_1 < 0.02$ nm and $0 < h_2 < 0.003$ nm, where the values of the norm have been chosen in several points to determine the first approach of the minimum of $D(\mathbf{V})$ by searching the minimum point of an appropriately fitted cubic spline to $D(\mathbf{V})$. Choosing fixed numbers of the most dominant intensities in every (h_1, h_2) point, the eqn (11) was constructed to calculate the values of the parameters $\langle u_x^2 \rangle$ and $\langle u_z^2 \rangle$. Completing the above described method we have received the optimized results of the new method: $h_1 = 0.01545$ nm, $h_2 = 0.0012$ nm. The five most important $DWfs$ (fitting to the five most dominant intensities) can be seen in Table 1 compared to García's results.[15] When we fitted the unknown parameters to the experimental results—con-

Table 1. The fitted Debye–Waller factors to the five most dominant measured intensities

$DWf_{(2,2)}$	0.307[a]	0.312[b]	−1.6%[c]
$DWf_{(2,0)}$	0.421	0.446	−5.9%
$DWf_{(2,1)}$	0.389	0.351	9.8%
$DWf_{(2,3)}$	0.208	0.218	−4.8%
$DWf_{(1,0)}$	0.533	0.533	0%

[a] The column of the results of the new inverse procedure.
[b] The column of the results of a traditional method.[15]
[c] The column of the relative errors between the two methods.
DWf denotes the Debye–Waller factor. See the text for the details.

sidering two, three, four or five most dominant intensities—the obtained values of the amplitude of the corrugation function and of *DWf*s were the same within ± 2 and $\pm 4\%$, respectively. Equation (2) is satisfied automatically within $\approx 5\%$. We should emphasize that García has obtained his results from several intensity distributions with different incident and azimuth angles of the He beam. The results show good agreement. In Table 1 the largest deviation of *DWf*s arises in the case of the reciprocal lattice vector (2, 1), but it is not too rough either. h_1 presents excellent agreement, but h_2 does not agree with García's corrugation parameters: $h_1 = 0.01535$ nm, $h_2 = 0.0017 \pm 0.0003$ nm.[15] However, the absolute error of the corrugation function [see eqn (4)] is not relevant ≈ 0.0005 nm. If we determine the Debye–Waller factors—dividing the experimental intensities with the intensities calculated by the fitted optimum corrugations parameters—we approximately obtain the values that García has calculated. This result backs up the identity of the two corrugation functions.

5. Conclusions

It has been shown that the computations underline the efficiency of the new model. This model demands only on experimental setup and preserves the correlation between the unknown parameters of the time independent model of TEAS and the unknown parameters of the Debye–Waller factors contrary to the traditional inverse procedures of TEAS.

Acknowledgements

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