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Progress in Automatic Structure Refinement with LEED

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It is demonstrated that conventional least squares optimisation techniques can be successfully used for automatic structure refinement with LEED. Examples are given for two adsorbate systems, H/Ni(110)-(1x2) and O/Ni(110)-(2x1) where rapid convergence is reached in a simultaneous optimisation of all structural parameters within the top three layers.

1. Introduction

The application of LEED as a standard technique for surface structure determination relies critically on its convenient use and its capability to solve complex structures. An automatic structure refinement technique, a clear recipe to localise the best fit model and a standardised criterion to judge the quality of the result would be most useful to make the method applicable by the non-specialist. Clearly, this situation has not yet been reached and, compared to X-ray diffraction, the method is still limited. Recent developments, however, show that considerable improvements are possible. The computational effort, which is still a limiting factor, can be reduced to a large extent [1-3]. Further improvements can be made introducing optimisation techniques into the structure analysis.

Several procedures have been proposed for an automatic structure refinement in which a minimisation of the conventionally used R-factors is obtained by gradient methods or search procedures [4-6]. The first approach had been proposed by Powell and de Carvalho [4], who applied a search procedure with an independent optimisation of each parameter. The method is generally applicable and does not require the calculation of derivatives. A more sophisticated method which allows the simulta-

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neous refinement of all parameters has been recently proposed by Rous, Van Hove and Somorjai [6]. This method is a gradient method which, in the formulation used there, also requires R-factor calculations only and no derivatives. A different approach, somewhat related to optimisation methods is the direct method proposed by Pendry, Heinz and Oed [5] in which the deviation from a reference structure is determined in one step. The procedure can be iterated if the linear expansion from the reference structure is not sufficient. The combination with Tensor LEED techniques [1] makes this method very efficient.

We propose here an alternative approach which closely resembles the methods conventionally applied in x-ray crystallography [7,8]. Both methods are diffraction techniques and the structure is usually determined by fitting model calculations to experimental data. The only difference in the two techniques is given by the way the experimental and theoretical data are compared, and, of course, in X-ray diffraction, further methods are applicable which cannot be applied with LEED. Using X-rays a set of diffracted intensities is measured at constant wavelength, while with LEED full spectra are measured and fitted to theoretical curves. The fit is usually done by adjusting the position of maxima and minima in the spectra.

There is a-priori no obvious reason why the simple comparison of relative intensities, which works well in the case of X-rays, should not work in the case of LEED. It should be noted that the position of maxima and minima in the spectra is not directly used. Measuring the distance between experimental and calculated spectra by the linear or quadratic deviation has the advantage that well developed optimisation techniques can be used. With the conventional R-factors, such as defined by Zanazzi and Jona [9] and Pendry [10] the fit-function becomes fairly complicated. A simpler R-factor therefore seems to be advantageous and it has indeed been shown that an R-factor based on the mean square deviation is well applicable and leads to reliable results. A full description of this method and the optimisation procedure has been published recently [7,8]. We therefore give here a short review of the novel structure refinement technique and discuss some calculational improvements in detail.

2. Optimisation procedure

The R-factors used in X-ray crystallography are either the linear or the mean square deviation between observed and calculated intensities at a fixed energy. The analogous approach in LEED has been proposed previously as the I(g) method [11]. The shortcomings of that method are that a superstructure producing only weak extra spots, such as a hydrogen superstructure, cannot be well determined because the I(E) spectrum of the superstructure spot is not properly weighted. This problem can be overcome by evaluating each beam with a separate weight factor. The R-factor is defined for discrete energies and is given by

$$R_{DE} = \sum_g W_g \frac{\sum_i |J^{ex}_{i,g} - c_g J^{th}_{i,g}|}{\sum_i J^{ex}_{i,g}} \quad ; \tag{1}$$

$$c_g = \sum_i J^{ex}_{i,g} / \Sigma J^{th}_{i,g} \quad ; \quad W_g = n_g / \sum_g n_g . \tag{2}$$

n_g is the number of points per beam g. This R-factor can be compared with the usual R-factor in x-ray diffraction. The quantity which is actually minimised in the optimisation procedure is, however, the mean square deviation R_2. R_{DE} is used for comparison with x-ray diffraction where the unweighted linear deviation is a standard R-factor.

To save computing time it is advantageous to choose a step width on the energy scale which is as large as possible. We have extensively tested which step width can be chosen without losing precision of the result. A step width up to 15 - 20 eV corresponding to about 10 -15 data points per spectrum seems to be completely sufficient [9,10]. The upper limit of the step width appears to be set by the requirement that enough points per beam remain.

Having defined the fit-function an automatic minimisation procedure can be introduced. A very efficient method has been developed by Marquardt [12]. His method combines the advantages of the gradient method and of the expansion method. In the gradient method the steepest decent of the R-factor in the parameter space is determined from its partial derivatives with respect to

all variable parameters. The method works well far away from the mimimum but converges only slowly near the minimum where the derivatives become very small. The expansion method, on the other hand, works well near the minimum and may lead to serious errors far away from the minimum.

In the expansion method a linear approximation of the intensity function is used

$$I^{th}(\underline{p}_0+\Delta\underline{p}) = I^{th}(\underline{p}_0) + \sum_{j=1}^{k} \left[\frac{\partial I^{th}(p_0)}{\partial p_j}\right] \Delta p_j + \ldots \tag{3}$$

where $\underline{p}_0 = (p_1,\ldots p_k)$ denotes the set of structural parameters and I^{ex}, I^{th} are the normalized intensities. Eq. (3) is inserted into the minimum condition

$$\partial R/\partial p_j = 0, \quad (j=1,\ldots k) \tag{4}$$

leading to a set of linear equations

$$\sum_{i=1}^{n} \{I_i^{ex} - I_i^{th}(\underline{p}_0) - \sum_{j=1}^{k} \frac{\partial I_i^{th}(\underline{p}_o)}{\partial p_j} \Delta p_j\} \cdot \frac{\partial I_i^{th}(\underline{p}_o)}{\partial p_m} = 0 \tag{5}$$

which is solved by matrix inversion

$$\Delta p = \beta \cdot \alpha^{-1} , \tag{6}$$

$$\beta_m = \sum_{i=1}^{n} (I_i^{ex} - I_i^{th}(\underline{p}_o)) \frac{\partial I^{th}(\underline{p}_0)}{\partial p_m}), \tag{7}$$

$$\alpha_{jm} = \sum_{i=1}^{n} \left[\frac{\partial I^{th}(p_0)}{\partial p_i} \cdot \frac{\partial I^{th}(p_0)}{\partial p_m}\right] . \tag{8}$$

The method of Marquardt replaces α_{jm} by

$$\alpha'_{jm} = \alpha_{jm} (1+\delta_{jm} \cdot \lambda) \tag{9}$$

δ_{jm} is the Kronecker symbol. If λ is large then the diagonal terms dominate and the result is similiar to the gradient method, if λ is small the expansion method is recovered. λ is dynamically adjusted by

$$\lambda = c \sum_{i=1}^{k} \left(\frac{\beta_i^2}{\alpha_{ii}}\right) \left(\frac{1}{R_2}\right) \tag{10}$$

The speed of the optimisation can be influenced by the parameter c.

3. Calculation of derivatives

The calculational effort in the procedure described above increases linearly with the number of free parameters because the numerical calculation of each derivative requires an additional full dynamical calculation per parameter at all energies. This calculation could be done very efficiently by applying the Tensor LEED technique [1]. However, an approximate calculation of derivatives seemed to be easier to implement in the existing program and turns out to be quite efficient. A linear approximation in calculating derivatives can be used.

The layer scattering matrices are approximated by:

$$M_{gg'} = M_{gg'}(\underline{p}_0) + \sum_j \frac{\partial M_{gg'}(\underline{p}_0)}{\partial p_j} \Delta p_j + \ldots \tag{11}$$

where $\partial Mgg'/\partial p_j$ can be obtained from a linear expansion of the inverse of the propagator matrix. The definition of the propagator matrix and the layer scattering matrices is given in ref. 13. In a linear expansion

$$\left[1-X(\underline{p}_0+\Delta\underline{p})\right]^{-1} = \left[1-X(\underline{p}_0)\right]^{-1} + \left[1-X(\underline{p}_0)\right]^{-1} \cdot \left[X(\underline{p}_0+\Delta\underline{p})-X(\underline{p}_0)\right] \cdot \left[1-X(\underline{p}_0)\right]^{-1} \tag{12}$$

and only matrix multiplications are required. The inverse of $\left[1-X(\underline{p}_0)\right]$ has been already calculated for the reference structure and can be reused again. Next an approximate calculation of the lattice sum is desirable. The sum over scattered waves from all atoms in the layer within a limiting radius of about 10 - 15 interatomic distances requires a good part of the computing time and it is worth while considering simplifications. The lattice sum of scattering paths between planes υ and υ' is

given by [13]

$$F^{\upsilon\upsilon'}_{\ell,m} = \sum_P i^{\ell} h_{\ell}(|k|\cdot|P+p_{\upsilon}-p_{\upsilon'}|)\cdot Y_{\ell m}(\Omega_{P+p_{\upsilon}-p_{\upsilon'}})e^{-ik(P+p_{\upsilon}-p_{\upsilon'})} \tag{13}$$

The sperical harmonics $Y_{\ell m}(\Omega_{P+p_V-p_{V'}})$ do not change much by increasing p_{υ} by Δp_{υ} and for the Hankel functions the asymptotic behaviour at large P can be used to calculate the derivatives for values $P > P_{min}$. P_{min} can be set to 3-4 interatomic distances without losing precision.

$$\frac{\partial h_l(z)}{\partial z} \approx ih_{\ell}(z) + e^{i(z-\ell\frac{\pi}{2}+\frac{\pi}{4})} \tag{14}$$

The lattice sum is therefore split up into two parts where only one part containing the near neighborhood of an atom needs to be recalculated. The minimum distance P_{min} can be chosen to about three interatomic distances. The calculational effort for the lattice sum is reduced by a factor of 15 by this approximation. The comparison of an approximate calculation of derivatives with the full dynamic calculation is shown in fig. 1.

The approximate calculation of derivatives turns out to be completely sufficient for all types of parameters.

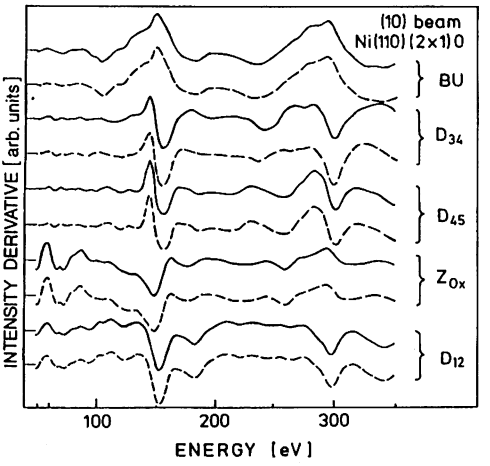

Fig.1. Comparison of approximate (dashed line) and full dynamical (solid line) calculation of derivatives. The structure parameters are displayed in fig. 2.

The increase of the speed of the calculation depends, however, on the number of variable parameters and the number of phase shifts used. In the examples shown below with 6 and 8 variable parameters a factor of 2.5 for the whole calculation is gained. Further improvements are possible. A linear expansion similar to that described in eq. (12) can be used for the matrices to be inverted in the layer doubling method.

4. Application to H/Ni(110)-(1x2) and O/Ni(110)-(2x1)

To illustrate the capability of the method the results of two adsorbate systems will be presented. Full structural results have been published recently [7,14,15], we present here only the results of the fit-procedure using the bulk values of Ni with a slight buckling in the third layer as start parameters.

The structure of the H/Ni(110)-(1x2) is shown in fig. 2; the hydrogen atoms are ignored in the calculation. The final structural parameters as well as the result of two calculations with different start parameters are given in table 1. The choice of the bulk structure as start parameter is not possible in this case. The bulk structure does not produce superstructure beams and the derivatives with respect to the superstructure parameters LS and BU vanish. The derivative vanishes because at a highly symmetry point two choices of the derivative are symmetrically equivalent. It is therefore necessary to shift at least one atom off its bulk lattice position.

A second example is O/Ni(110)-(2x1). The structural model is shown in fig. 3. Here 6 independent parameters within the top three layers had to be refined, assuming

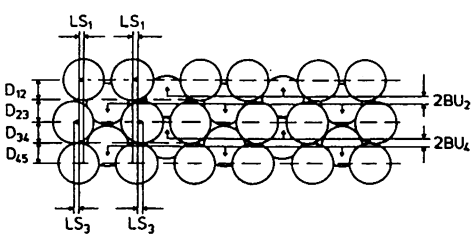

Fig. 2. Model of the (1x2) structure of H/Ni(110). Hydrogen atoms are not shown.

Table 1. Result of a simultaneous fit of 8 structural parameters. The final structure was reached after 10 iterations, R_{DE} = 0.3

Parameter	Start Value	Final Value [Å]
D_{12}	1.246	1.223
D_{23}	1.246	1.331
D_{34}	1.246	1.272
D_{45}	1.246	1.220
LS_1	0	0.30
LS_3	0	0.12
BU_2	0.1	0.25
BU_4	0	0.02

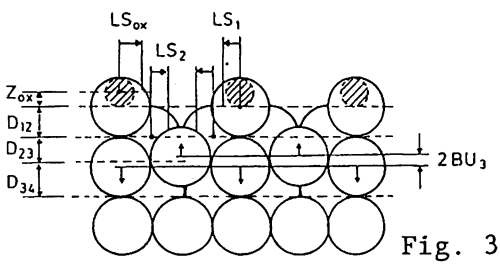

Fig. 3 Model of O/Ni(110)-(2x1)

Table 2. Result of a simultaneous fit of 6 parameters, the minimum R-factor was reached after 7 iterations, R_{DE} = 0.24

Parameter	Start Value	Final Value [Å]
Z_{ox}	0.3	0.224
D_{12}	1.246	1.293
D_{23}	1.246	1.246
LS_2	0	0.011
BU_4	0	0.052

that oxygen sits in the symmetric position. Results are shown in table 2. 15 eV steps were used in the energy range between 40 and 340 eV, corresponding to 106 data points in 8 I/V spectra.

In the above calculations oxygen was fixed in the symmetric site. A detailed study showed that a slight preference was found for an asysmmetric site [14]. The search

for an asymmetric site was stimulated by a HREELS study [16] which showed an additional oxygen mode not compatible with the assumption of a symmetric oxygen position. This asymmetry has been neglected here, because it is felt that from the LEED data at normal incidence alone this asymmetry cannot be definitely concluded [14]. The influence of a lateral shift of the oxygen atom on the other structural parameters can be neglected.

5. Discussion

A central point in any optimisation scheme is of course the radius of convergence within which a minimum will be localised. That the minimum may be a local mimimum has been already pointed out. Local minima can be avoided only by choosing start structures on a wide grid in the parameter space. The radius of convergence therefore determines the grid size which must be applied to exclude local minima. This same problem occurs, by the way, in the conventional R-factor analysis. The average distance between local minima in the R-factor hyperface may be estimated to be about 0.5 Å. This results from the simple consideration that with an average wavelength of 1.0 Å an interference maximum of backward and forward scattering between two atoms occurs again after a shift of 0.5 Å. It follows that roughly a deviation of 0.2 - 0.3 Å can be tolerated in the start parameters. This is a rough estimate, of course, and applies to parameters parallel to $\Delta\underline{k}$. Smaller distances between local minima may also occur due to domain averaging [6].

To check the radius of convergence we performed several runs with different start values for two parameters in the O/Ni(110)-(2x1) structure, Z_{ox} and D_{12}, keeping all other parameters at their optimum value. The results are shown in table 3.

It may be concluded that the radius of convergence is about 0.2 Å in agreement with the estimate considered above. In test runs with a simultaneous fit of all parameters the same radius of convergence was found which indicates that the parameters are only weakly correlated.

The convergence depends also on the parameter c in eq. 10, this has been chosen as 0.2 in the above examples. A larger value decreases the speed of the calcula-

Table 3 Check of the radius of convergence for two parameters.

	start	final	R_{DE}	No. of iterations
Z_{ox}	0.5	0.83	0.43	6
Z_{ox}	0.4	0.22	0.243	4
D_{12}	1.5	1.58	0.73	1
D_{12}	1.4	1.31	0.242	3

tion and has been found sometimes to increase the radius of convergence because the large steps in the beginning of the iteration process are damped.

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