Surface Science 219 (1989) L637–L645
North-Holland, Amsterdam

SURFACE SCIENCE LETTERS

A NOVEL PROCEDURE FOR FAST SURFACE STRUCTURAL ANALYSIS BASED ON LEED INTENSITY DATA

G. KLEINLE

Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-1000 Berlin 33, Germany

W. MORITZ

Institut für Kristallographie und Mineralogie, Universität München, D-8000 München 2, Fed. Rep. of Germany

D.L. ADAMS

Institute of Physics, University of Aarhus, DK-8000 Aarhus, Denmark

and

G. ERTL

Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-1000 Berlin 33, Germany

Received 19 April 1989; accepted for publication 1 June 1989

By evaluating LEED intensities from different diffraction beams taken only at discrete energy intervals (which may be as large as 15–20 eV) the same degree of reliability in surface structure determination can be reached as with the conventional techniques based on analysis of continuous I/V-spectra. The minimum of the corresponding R-factor can be found by a least-squares fit method, as will be exemplified with a system in which 8 structural parameters were subject to simultaneous refinement.

Low energy electron diffraction (LEED) is still the most powerful technique of surface crystallography – despite the recent advent of other methods such as the scanning tunneling microscope – and numerous surface structures have already been solved in this way [1–4]. Unlike with X-ray diffraction, however, a surface structural analysis based on LEED intensities will always be the result of a trial strategy, in which intensity/voltage (I/V)-data calculated for an assumed structure have to be compared with experimental data until the best agreement is reached. The computational effort increases very strongly with the number of atoms within the surface unit cell as well as with the number of structural parameters, and hence so far mostly only relatively simple structures were solved. Recent progress in attempts to reduce the

computing time includes the introduction of symmetry adapted functions in the electron propagator matrices which enables the reduction of the number of atoms in the unit cell to the number of symmetrically unequivalent atoms [5], as well as the development of the Tensor LEED technique which allows fast variation of structural parameters within certain limits [6].

The present paper will describe a novel procedure by which this computational effort can be reduced drastically, so that also more complex structures will become accessible to routine analysis in the future. For illustration of the power of this technique we will present an example for which the structure could be solved in terms of 8 (!) freely adjustable structural parameters. The solution of such a complex problem is enabled essentially (i) by neglecting redundant information, and (ii) by applying an efficient algorithm for optimising the model structures leading to rapid convergence. This aspect is of major importance and is enabled by the introduction of an R-factor similar to that used in conventional X-ray crystallography.

A typical LEED experiment yields continuous I/V-spectra for a small number of diffraction beams. Calculation of the spectra is usually performed at energy intervals between 1 and 5 eV, which small step widths then ascertain reliable interpolation. The degree of agreement between calculated and actual intensity data is expressed in terms of R-factors which are evaluated from comparison of weighted integrals over the continuous I/V-spectra. Mainly two R-factors, introduced by Zanazzi and Jona (R_{ZJ}) [7] and by Pendry (R_P) [8], respectively, are commonly in use, but a mixture of such R-factors could be successfully applied as well [9]. A more general approach for comparing spectra is based on using metric distances [10], and it was found that in this case reliable results may be obtained even with energy steps of 8 eV [11]. The mean square deviation represents the simplest approximation along these lines. This method was also successfully tested previously [12], but did not find further widespread application. The general philosophy has been that matching of peaks in experimental and theoretical I/V-spectra is the most important criterion, which requires calculation of a large number of data points and renders automatic search for the R-factor minimum very cumbersome.

The situation is quite different in X-ray structural analysis: Here the intensity relations between different diffraction spots taken at a fixed energy are compared with corresponding theoretical data. This concept had also been introduced into LEED crystallography ($I(g)$ method) [13] and was demonstrated to work well in certain cases [14], but did not find more widespread use because of several shortcomings, e.g. concerning inappropriate representation of spots with weak intensities as well as systematic experimental difficulties in determining *absolute* intensities. This approach works, however, with a much smaller set of data points. In conventional X-ray analysis typical only $(5-10)x$ intensity data are required, if x is the number of structural parameters to be determined. (For LEED a somewhat larger set of data seems to be necessary,

since usually only few beams with small momentum transfer parallel to the surface can be recorded experimentally.) These considerations lead to the conclusion that a considerable reduction of the number of LEED intensity data should be possible without substantial loss of information. In fact, the total information stored in a LEED I/V-spectrum is partly redundant: It consists of a superposition of Lorentzian peaks of approximately equal width and can be restored from a small set of numbers representing the energies and heights of these (possibly overlapping) peaks [15]. However, rather than to reduce the I/V-data to these peak parameters which then would have again to be retraced in the calculated spectra, a more general procedure proved to be rather successful as will be outlined now.

The basic philosophy is to treat LEED intensities for various spots g only at discrete (equally spaced) energies i, rather than to evaluate continuous I/V-spectra. Comparison between experimental and theoretical data is achieved through the R_{DE}-factor (DE = "discrete energies") defined as

$$R_{\mathrm{DE}} = \sum_g W_g \frac{\sum_i \left[I_i^{\mathrm{ex}} - C_g I_i^{\mathrm{th}} \right]}{\sum_i I_i^{\mathrm{ex}}} .$$

First the summations Σ are performed over the n_g data points (at energies i) for each beam g, whereby the scaling factor $C_g = \Sigma I_i^{\mathrm{ex}} / \Sigma I_i^{\mathrm{th}}$ normalises the intensities I_i of the individual beams. This ansatz also eliminates eventual systematic experimental errors and avoids underestimation of contributions from beams with weak total intensity. Then the contributions from the individual beams are weighted with the factor $W_g = n_g / \Sigma n_g$ and summed up over all beams g.

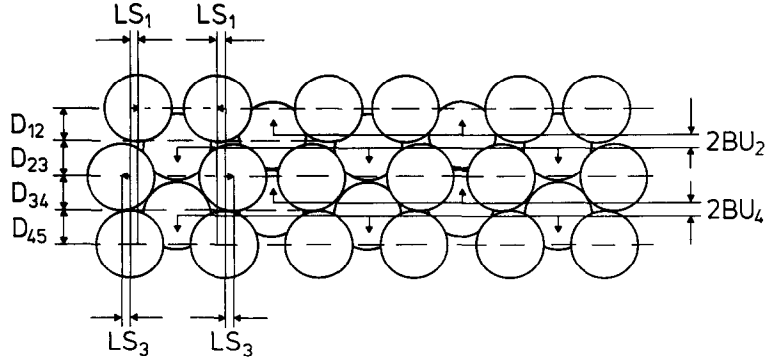

Fig. 1. Model of the H/Ni(110)-1×2 structure. Cut along the (110) plane, H atoms omitted. The atomic positions within the topmost two layers are drawn on scale. The actual displacements within deeper layers are much smaller than depicted (see table 1).

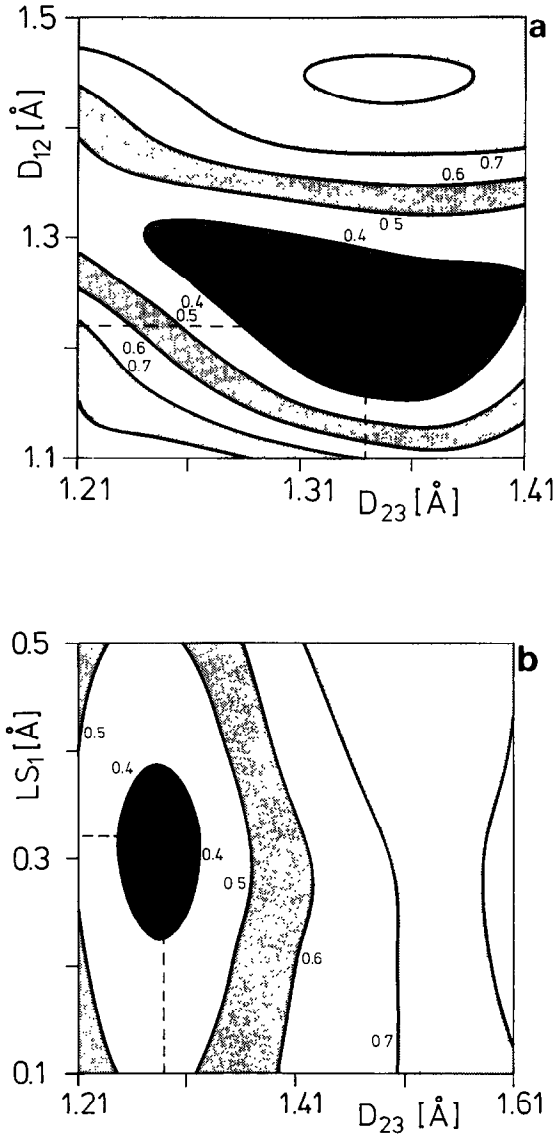

Fig. 2. Contour plots for the R_{DE} factor upon variation of various structural parameters. The R_{DE}-minimum is marked by □; ⊕ and ⊗ mark the minima of the corresponding R_{ZJ}- and R_P-values, respectively. (a) Variation of the interlayer separations D_{12} and D_{23}. (b) Variation of the lateral shift within the first layer, LS_1, and of the separation between the second and third layer, D_{23}. (c) Variation of the "buckling" in the second layer BU_2 and of the separation between the third and fourth layer, D_{34}.

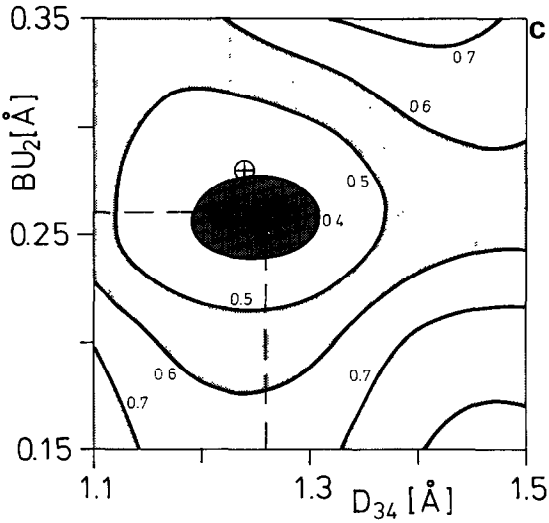

Fig. 2. Continued.

Extensive tests demonstrated that the results of conventional R-factor analyses could be reliably reproduced by this approach even with an energy grid of 15 to 20 eV and a total number of 5 to 10 intensity data per diffraction beam. That means a total number of about 100 data points suffices for a structural analysis.

This result will be exemplified with the "row pairing" 1×2-structure of Ni(110) formed by saturation with adsorbed H atoms at $T < 180$ K. This system was chosen for test purposes because its structure had previously been determined by conventional R-factor analysis to a very degree of reliability [16]. In addition, it turned out that the novel optimisation search to be described below permitted even analysis of lattice distortions in the third and fourth atomic layers, which otherwise would hardly have been accessible. The structure to be discussed originates from an adsorbate-induced reconstruction. Because the adsorbate (H) is a weak scatterer, its contribution to the recorded LEED intensities is completely negligible in this case, as verified in extended test calculations. For this reason the structural model reproduced in fig. 1 shows only the Ni atoms. The atomic positions in the first ("row pairing") and second ("buckling") layers are drawn on scale, while the distortions in the third and fourth atomic layers had to be strongly exaggerated in order to become visually detectable (see below). In figs. 2a–2c contour plots of the R_{DE}-factors in dependence of 5 structural parameters are reproduced, namely the spacings between the first three atomic layers, the lateral displacement within the first layer (LS), and the "buckling" in the second layer (BU). All other structural parameters were kept at their bulk values. In this case an

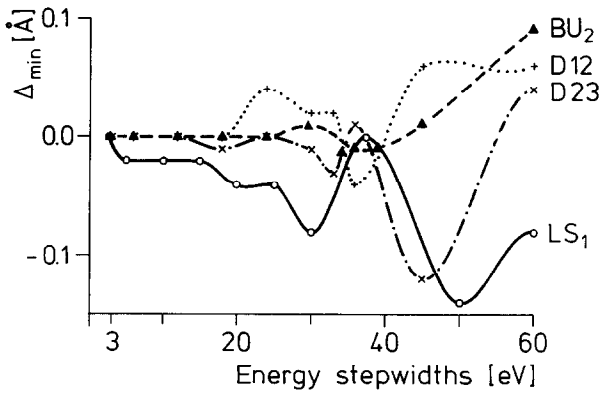

Fig. 3. Deviations of the "best fit" of various structural parameters from their optimum value as a function of the step width on the energy scale. The optimum value was determined with a step density of 3 eV by analysing 480 data points from 11 beams. An increase of the step width to 15 eV reduces the computational effort by a factor of 5 without any significant loss in accuracy.

energy grid of only 3 eV was used, which was equally applied for evaluating the conventional Zanazzi–Jona and Pendry R-factors, respectively, whose minima are also marked in these figures. The close agreement to within ± 0.02 Å demonstrates that all three methods are able to produce structural information to within the same degree of accuracy.

Next we check how the "best" values for different structural parameters determined by the R_{DE} strategy vary with the width of the energy steps of the intensity data used for the analysis. Fig. 3 shows the resulting deviations Δ_{min} of the "best fit" data for varying step width from the data presented before as derived with a 3 eV energy grid. As can be seen, considerable deviations occur only for step widths > 15 eV! Similar conclusions were reached for other systems, namely the clean Ni(110) and Pd(110) surfaces as well as the H/Pd(110)-1 $\times$ 2 structure. In the latter case only fairly good agreement between experimental and theoretical data had previously be reached following conventional R-factor analysis [17], but nevertheless this result was perfectly reproduced by the R_{DE} method. A reduction of the computational effort by a factor 3–5 is already reached at this stage.

For a set of statistically independent data points, reduction of the data base would of course lead to a loss of accuracy for any quantity derived from these data. However, the data points forming LEED I/V spectra are correlated with each other: These may be approximated by a superposition of Lorentzian peaks, whereby even different peaks are not statistically independent from each other due to their common physical origin. As long as the accuracy to be achieved is limited by approximations underlying the calculations (uniform damping, isotropic amplitudes, muffin tin potentials etc.) as well as by

experimental errors (noise, absolute intensities, etc.), it will not be affected by data reduction to any significant extent. Up to a step width of 15 eV, corresponding to about ten times as many data points as independent parameters, the locations and depths of the R-factor minima remain essentially unchanged. Only for even coarser energy grids the data reduction becomes the limiting factor and the accuracy will be lowered.

As a main step in further optimising the computational effort, the incorporation of an automatic search procedure for the "best fit" is straight forward. The use of the mean square deviation allows the use of standard optimisation procedures. First attempts to apply automatic structure refinements have been proposed by Cowell and Carvalho [18] using a search routine for the minimum in the conventional R-factor analysis. Another procedure was proposed by Rous and Pendry [19] in terms of the Tensor LEED technique in a gradient method.

In the course of the present work it was found that a least-squares fit procedure with simultaneous refinement of all structural parameters works exceedingly well. A non-linear optimisation scheme [20] was used which has the advantage that the step width in the parameter refinement is feedback-adjusted and thus provides rapid localisation of the minimum. The least-squares fit procedure requires the calculation of the derivative $\mathrm{d}I/\mathrm{d}x$ for each energy point. In future development of the approach presented here this might favourably be achieved by adopting the Tensor LEED technique [6]. In the present stage these derivatives were calculated just numerically.

The reduction of the computational effort is obvious for structures with a large number of freely adjustable parameters. The optimisation of n parameters using a grid in the parameter space requires at least a number of 3^n I/V curves. Even if a block refinement is used, where only a certain number of parameters is refined independently, a structure with, say, 20 parameters is not solvable in that way. A simultaneous refinement of all parameters requires $i(n+1)$ calculations, where i is the number of iterations, usually in the order of 10.

The results of *simultaneous refinement* of all the 8 parameters indicated in fig. 1 are listed in table 1. For these calculations in total 86 data points from 11 diffraction beams with an energy grid of 15 eV were used. The optimisation was started from the bulk structure with the only exception that a buckling in the second layer by 0.1 Å was assumed. It is of course necessary to start with a

Table 1
Optimum structural parameters (in Å) for the H/Ni(110)-1×2 system (fig. 1) yielding $R_{\mathrm{DE}} = 0.30$ (the interlayer spacing in the bulk is $D_{\mathrm{bulk}} = 1.246$ Å)

LS_1	BU_2	LS_3	BU_4	D_{12}	D_{23}	D_{34}	D_{45}
0.30	0.25	0.12	0.02	1.24	1.33	1.27	1.22

structure which exhibits the symmetry of the superstructure. The "best fit" (i.e. the minimum R_{DE}-factor) was reached after 10 iteration steps. Starting the calculation from the totally undisturbed bulk structure led to a local minimum. A reliable criterion for the average radius of convergence for structural parameters cannot be given at the present stage because of lack of experience with different structures, but we do not expect significant differences to the conventional R-factor analysis.

For the final structure model the full I/V-spectra were calculated for comparison with the previously published results [16]. Inclusion of the three additional structural parameters from the deeper layers caused reduction of R_P from 0.38 to 0.29, and of R_{ZJ} from 0.15 to 0.13, respectively, i.e. still a noticeable improvement.

The scheme proposed here was applied to the structural analysis of various other systems, namely clean Cu(110) and W(100)-c2 × 2, as well as the O/Ni(110)-2 × 1 structure for which the "missing row" model could be confirmed [21]. In all these cases – starting from the bulk structure – the optimum structural parameters were reached after about five to ten iteration steps. (If both the structural parameters as well as the inner potential were refined, the convergence was slower, as expected.)

The optimum value for $R_{DE} = 0.30$ is comparable with the R-factors obtained in conventional X-ray crystallography for the correct structure without further refinement due to anisotropic thermal vibrations [22]. In analysis of LEED intensity data so far only isotropic thermal vibrations are included, but there are good prospects that with future LEED structural analysis a similar degree of precision may be reached as with X-ray crystallography.

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