Recent advances in LEED surface crystallography

K. Heinz *, M. Kottcke, U. Löffler, R. Döll
Lehrstuhl für Festkörperphysik, Universität Erlangen-Nürnberg, Staudtstr. 7, D-91058, Erlangen, Germany

Received 15 August 1995; accepted for publication 31 October 1995

Abstract

After the arrival of fast, reliable and computer controlled measurement techniques the main obstacle in LEED structure determination was the vast computational work necessary to calculate dynamical intensities and to retrieve the correct structure. This has been largely overcome by structural search procedures and in particular by the introduction of the perturbation method tensor LEED. The power of this development is reviewed with emphasis on recent extensions to describe the easy chemical substitution of atoms and their anharmonic and anisotropic vibrations. Additional to surfaces of considerable geometrical complexity (geometrical tensor LEED), also fast access to substitutionally disordered compounds with the layer dependent determination of their surface stoichiometry (chemical tensor LEED) is allowed. Also, there is access to surface dynamics (thermal tensor LEED). Additionally, tensor LEED can be inverted to establish a direct method for the direct determination of the surface stoichiometry and the geometrical refinement of structures without application of trial-and-error procedures.

Keywords: Low energy electron diffraction (LEED); Surface structure

1. Surface structure determination by LEED

The quantitative determination of surface structures by low energy electron diffraction (LEED) started in the early seventies when considerable efforts to develop a full dynamical scattering theory had been successful [1]. This marks the start of surface crystallography. Though up to-day a number of other surface structural tools have been developed, the lion's share of known structures came by LEED which still keeps to be the leading method. This is mainly due to the fact that LEED – different from most other methods – allows the retrieval of the full surface structure and not only of special features as e.g. bond lengths or top layer atom positions.

As true for any diffraction technique, calculated model intensities have to be fitted to experimental data in order to retrieve the structure. So, the problem of structure determination is threefold: First, reliable data have to be measured. Second, accurate intensities must be calculated for a promising structural model. And last but not least, the correct structure must be retrieved by variation of model parameters in order to find the best theory–experiment fit. None of these tasks is trivial. However, by today's standards the experiment seems to be the least critical task: Sophisticated measurement techniques are available which easily and in a half-automated way yield reliable intensity spectra. Most laboratories use computer controlled video cameras which detect the light generated by diffracted electrons on a luminescent screen, but also position sensitive devices for electron detection.
are in use (for a recent review see Ref. [2]). By their speed and sensitivity the methods minimize the influence of residual gas adsorption and of electron induced desorption or cracking of adsorbates. They allow fast multiple measurement of data to improve the signal-to-noise ratio as well as equivalent beam averaging in order to reduce the influence of sample misalignment. Intensity spectra for a selected set of beams can be obtained within minutes. A recent and commercially available version of the video technique is operated by a 80486 PC with the full diffraction image digitized at each energy [2]. Different functions as the measurement of diffuse background distribution, of spot profiles or integrated spot intensities can be chosen and controlled by mouse or keyboard driven menus. Fig. 1 displays an example.

The ease with which experimental data can be measured is in some contrast to the two remaining tasks of structure determination. Due to the strong multiple scattering of low energy electrons the computer codes for the calculation of intensities for a certain structural model are rather complex and require substantial amounts of computer time even on powerful computers. This is the price to be paid for the unique property of LEED providing the full surface structure. In addition and even worse, however, the final task, i.e. the search for the correct structural model can be rather tedious, time consuming and even unsuccessful, in particular when complex structures are the subject of investigation. The problem is illuminated best, if one considers a structure with N coordinates of atoms in the surface unit cell to be determined.

Fig. 1. Menu driven automated image data acquisition system operated under the control of a personal computer (AIDA-PC). Additional to the digitized LEED pattern a spatial intensity profile along a cut through the pattern is displayed.
With $M$ trial values for each of these parameters to be tested, the number of test structures and so full dynamical LEED intensity calculations amounts to $M^N$. For a structure of medium complexity, say with five atoms in the unit cell ($N = 15$) and $M = 5$ trial values for each coordinate, there are about $3 \times 10^{10}$ structures to be tested. It is obvious that this is impracticable.

Computational efforts to get around this problem must be twofold: An efficient procedure for the structural search is needed which avoids the scan of the parameter space, and the time necessary to calculate the intensities for a certain trial structure should be minimized. In the following, recent progress made with respect to these needs is reviewed together with the application to the determination of rather complex structures. Emphasis is on the description of the perturbation method tensor LEED which allows fast access to intensities of structures neighboured in parameter space. Its application to geometrically, chemically and thermally related structures is described in the next two sections. Section 4 reports on the use of effective search procedures and describes the possibility to invert tensor LEED in order to establish a direct method. The progress recently made is summarized in the final section.

2. The concept of tensor LEED: geometrical tensor LEED

Though theory and computer codes for the intensity calculation are well established [1,3], their application suffers from a considerable drawback: For each trial structure the full calculation has to be repeated more or less from scratch, even if the corresponding parameter values differ by only small amounts. The variation of intensities with such small changes of parameters is illustrated in the bottom panel of Fig. 2. The full curves represent intensity spectra of a beam of the adsorption system $c(4 \times 2)$-K/Ni(100) for various values of the adsorption height $d_{01}$ as displayed in the upper panel. With the choice of a 0.1 Å step width for $d_{01}$ the spectra change smoothly from step to step, though details of the spectra as well as peak positions can change markedly. This puts the question whether the spectra for a parameter set neighboured to a certain reference can be calculated by perturbation of the reference spectra rather than by a fully new computation in each case.

The answer is yes and is given by the perturbation method tensor LEED whose development started about ten years ago [4] and yet after various improvements and methodological extensions [5–8] cannot be considered complete (for recent reviews see Refs. [2,9–11]). Tensor LEED calculates the electron wave field $|\psi(E,k_f)\rangle$ within the sample generated by an electron beam incident with energy $E$ and surface parallel momentum $k_f$. This is for a certain structure which we call refer-
ence structure in the following. Of course, with the wave field known also the diffraction amplitudes are known as usual. Now, however, imagine that a certain atom at position \( r_j \) and with scattering matrix \( t_j \) is displaced to the position \( r_j + \delta r_j \), so that a new structure results.

If we describe the scattering of the displaced atom by a scattering matrix \( t'_j \) with reference to the original position \( r_j \), the change of the scattering matrix is simply

\[
\delta t_j(\delta r_j) = t'_j - t_j.
\]  
(1)

In angular momentum representation \( \delta t_j \) can be expressed by

\[
\delta t_{jLL'} = \sum_L G_{LL'}(\delta r_j)t_{jLL'}G_{L'LL}(\delta r_j^{-1}) - t_{jLL},
\]  
(2)

with \( L = (l,m) \) the angular momentum and magnetic quantum numbers and \( G \) the spherical wave propagator. Due to the displacement both \( \delta t_j \) and \( t'_j \) are non-diagonal in contrast to the original matrix \( t_j \). The displaced atom causes a change \( \delta A \) of the diffraction amplitude which for the final direction with parallel momentum \( k_{fj} \) can be calculated by first order perturbation yielding for a set \( \{j\} \) of displaced atoms:

\[
\delta A = \sum_j \langle \Psi(E, k_{fj}) | \delta t_j | \Psi(E, k_{fj}) \rangle,
\]  
(3)

which in angular momentum representation formally can be written as

\[
\delta A = \sum_j T_{jLL'} \delta t_{jLL'},
\]  
(4)

yielding the intensity \( I = |A_0 + \delta A|^2 \) of the new structure with \( I_0 = |A_0|^2 \) the intensity of the reference structure. \( T_{jLL'} \) is a tensor explaining the naming tensor LEED or, more precisely because of geometrical displacements involved, geometrical tensor LEED. The tensor is fully determined by the reference structure and so, computed once by use of Eqs. (2)–(4), allows the fast access to trial structures neighboured to the reference. As obvious from Eq. (4) the perturbation is kinematic, i.e. multiple diffraction between changes of scattering matrices is ignored.

This raises the question to which extent atoms can be displaced with tensor LEED still being a good approximation. As the complexity of multiple scattering inhibits a theoretical error estimation, only experience can tell about the limits of validity. They depend on the amount and direction of displacements, on the scattering strength and number of atoms displaced and in a very complex way on correlations between them. As a crude rule, displacements up to about 0.4 Å for scatterers of medium strength mark the limit of geometrical tensor LEED. A demonstration is given in Fig. 2 where broken line curves are calculated by tensor LEED for different adsorption heights of K on Ni(100) with the reference calculation made at \( d_{01} = 2.68 \) Å. The comparison to the exact curves is excellent though for larger displacements rather drastic changes compared to the reference are observed. The quality of the agreement is also mirrored by the Pendry R-factor [12] given at the right of each pair of spectra. For displacements of 0.4 Å the agreement is still satisfying but for larger values intolerable deviations must be expected.

Of course, the real power of tensor LEED comes by application to complex structures, in particular when they are caused by displacements of atoms in a simple reference. An impressive example is that of the epitaxial growth of Fe on Cu(100) by which fcc-Fe can be produced [13,14]. At about 4 monolayers of iron already the diffraction pattern tells by the appearance of a 5 × 1 superstructure that the structure must be more complex than a simple continuation of the fcc substrate. In fact, the systematic variation of all atomic positions in the 5 × 1 unit cell and in all 4 layers off the ideal fcc positions in directions vertical and parallel to the layers retrieves the correct structure. This is equivalent to the determination of as much as 40 atomic coordinates. As the off reference displacements are below 0.4 Å this is an ideal application of geometrical tensor LEED (for more details of the structure determination see Refs. [14,15]).

3. Chemical and thermal tensor LEED

Though tensor LEED was originally designed to describe the geometrical perturbation of a surface, inspection of Eq. (1) tells that \( \delta t_j \) must not necessarily be due to a geometrical displacement. It might come by any change of the atomic scatter-
ing conditions, in particular by the substitution of one atom (type A) by another (type B) as described by

$$\delta t_j = t_j^B - t_j^A,$$

(5)
i.e. by a chemical change of the surface (chemical tensor LEED). It can be used to substitute adsorbed atoms, to introduce vacancies in a certain structure ($\delta t_j = -t_j$) or to create otherwise partial disorder in a surface [2,16]. Also, it is suited to describe perturbatively the non-spherical scattering of atoms when covalently bound [8]. Yet, the most important field of application is the variation of the layer dependent concentration of scatterers in substitutionally disordered compounds, in particular of alloys: If in a layer $j$ the concentration and scattering matrix of a species A is $c_j$ and $t^A$, respectively, and $(1-c_j)$ and $t^B$ the corresponding quantities for species B, the average atomic $t$-matrix of the layer is $t_j = c_j t^A + (1-c_j) t^B$. This “average $t$-matrix approximation” (ATA) works very well for disordered compounds [17]. If, with respect to a certain reference stoichiometry the concentration is changed by $\delta c_j$, the corresponding change of the average scatterer in layer $j$ is

$$\delta t_j = \delta c_j (t^A - t^B)$$

(6)

and by use of Eq. (4) the intensities for the new structure can be calculated with ease.

Fig. 3 demonstrates the validity of chemical tensor LEED for the (100) surface of the substitutionally disordered alloy Fe$_{90}$Al$_{10}$. As well known, at such surfaces segregation of some of the constituents may occur at the surface leading to its enrichment in the first few layers. Intensity spectra for such segregations are simulated in Fig. 3 whereby full and broken line curves represent full dynamical and tensor LEED calculations, respectively. Whilst the bottom spectrum corresponds to the bulk terminated sample taken as the reference, the middle pair of curves corresponds to aluminum segregation $c_1 = c_2 = 50\%$, the top pair to $c_1 = c_2 = 100\%$ in the first two layers. As obvious, full dynamically calculated spectra agree very well with data obtained via chemical tensor LEED. This is even true for $c_1 = c_2 = 100\%$ for which the spectra change dramatically with respect to the reference. This makes chemical tensor LEED an effective tool for the fast determination of the layer depen-
dent stoichiometry of substitutionally disordered compounds. In fact the method has been applied in this sense quite successfully [18–21]. The large range of validity means that any trial concentration can be reached. So, there are no limits of application, in contrast to geometrical tensor LEED. This may be due to the fact that $\delta t$ in Eq. (8) is exact with no propagators involved.

The change $\delta t$ might also come by atomic thermal vibrations in – or decreased with respect to – a certain reference. This thermal tensor LEED method is very advantageous because it makes repeated calculations with different temperature corrected sets of phase shifts unnecessary. So, e.g. for isotropic vibrations at temperature $T$, the surface Debye temperature $\Theta$ can be easily fitted using $\delta t = \delta t(T, \Theta)$ and this can even be done for each layer separately [6]. An example is given in Fig. 4 which displays the Pendry $R$-factor map for clean Ni(100) with the Debye temperatures $\Theta_1$ and $\Theta_2$. 

![Fig. 3. Calculated spectra of the 10 beam for the (100) surface of the substitutionally disordered alloy Fe$_{90}$Al$_{10}$. Full and broken lines correspond to data calculated full dynamically and via chemical tensor LEED, respectively. The bottom curve represents the bulk terminated surface which is taken as the reference stoichiometry. The next two pairs of spectra correspond to aluminum segregation $c_1 = c_2 = 50\%$ and $c_1 = c_2 = 100\%$ in the first two layers.](image-url)
for the first two layers fitted. The best fit results for $\Theta_1 = 250$ K and $\Theta_2 = 350$ K which demonstrates that the Debye temperature approaches the bulk value $\Theta_b = 440$ K layerwise step by step.

Moreover, anisotropic and anharmonic vibrations can be handled by thermal tensor LEED too [7]. This can be realized by replacing $\delta r_j$ in Eq. (2) by vibrational displacements followed by proper averaging to yield the $t$-matrix change correcting for vibrations. As an example, the application of the method to the hollow site adsorption of K on Ni(100) showed that the vibrational amplitude of potassium atoms parallel to the surface is about 10 times as much as normal to it ($u_\parallel = 0.5$ Å, $u_\perp = 0.05$ Å) [7]. The quality of the theory–experiment fit is improved markedly [7]. A similar improvement was found by a more conventional treatment of anisotropic vibrations for $(\sqrt{3} \times \sqrt{3})R30^\circ$-CO/Ru(0001) for which a lateral vibrational amplitude of 0.4 Å was found for oxygen [22].

4. Structural search procedures and direct methods

With the measurements done and the computer codes for fast intensity calculations available, the probably most demanding step of the structure determination still needs to be done, i.e. the retrieval of the correct structure by finding the best fit position in the multidimensional parameter space. The methodically easiest way certainly is the scan of the parameter space which is still successfully practised in many cases. However, as pointed out in the first section, this is tedious and eventually becomes impracticable when with the increasing complexity of structures more and more parameters have to be determined. Then there must be a strategy to find the best fit avoiding the unnecessary test of a vast amount of parameter sets.

One of the strategies successfully developed in recent years is the automated search in parameter space. A number of procedures were developed in recent years differing in requirements, numerical strategy and efficiency (for recent reviews see Refs. [2,23]). Generally and described in a simplified way, they start at a certain preselected point in parameter space and explore the surrounding part to find a direction in which the R-factor decreases. After acceptance of a new point this procedure is iterated until convergence is reached. However, one might end in a local rather than in the wanted global minimum of the R-factor. To avoid this, the starting structure has to be varied statistically. If all starting structures lead to the same final best fit, there is a high probability that this corresponds to the correct structure. For the intensity calculations both conventional schemes [24–27] as well as tensor LEED [28] are used. The combination of the automated search with tensor LEED seems to be the most efficient procedure though care must be taken not to go beyond the accuracy limit of tensor LEED but perform new reference structure calculations when necessary. The problem of landing in a local rather than in a global minimum for the R-factor also may be overcome by using simulated annealing algorithms as proposed recently [29]. Its combination with the above described method of steepest descent was found to work in the most effective way. In principle simulated annealing can also be applied with the additional use of tensor LEED avoiding full dynamical calculations at each of the statistically chosen grid points. Again care has to be taken with respect to the validity limits of tensor LEED. We developed a simplified version which simulta-
neously uses both geometrical and chemical tensor LEED [30]. As an example Fig. 5 displays the model structure found by this procedure for c(2×2)-C/Mo_{75}Re_{25}(100) with carbon adsorbed in 4-fold hollow sites and a second layer buckling induced by adsorption (for details see Ref. [31]). A total of 9 parameters including the stoichiometry in the first three substrate layers were fitted allowing for the test of about 10^{15} trial structures. By the procedure applied only some 1000 of them have to be probed as displayed by the R-factor convergence in the bottom panel of Fig. 5. It should be pointed out that even considerably more complex structures with more than 10 atoms in the surface unit cell have been solved by the combined application of search procedures and tensor LEED. An example is given in Fig. 6 for the coadsorption system (3×3)-(C \_6H_6 + 2CO)/Rh(111) for which distortions both in the substrate and the species adsorbed were detected [32]. For a recent review of complex structures solved see Ref. [2].

The second strategy to retrieve the correct structure is to invert measured intensity data directly by the inversion of tensor LEED [33–36]. This works whenever tensor LEED is linear or can be linearized with respect to the quantity wanted, which can be an atomic displacement δx_j (or δy_j, δz_j), a change of concentration δc_j or an unknown vibrational amplitude change δu_j, whereby all these quantities are zero in the reference structure. If we denote by δp_j any of these parameter changes and assume δt(δp_j) ≈ δp_j to hold, the corresponding change of the diffraction amplitude δA_g = \langle A_g - A_{g0} \rangle, with g labelling both beam and energy, writes as

$$\delta A_g = \sum_j T_{gj} \delta p_j.$$  

Assuming the intensity change being small, the new intensity can be written as

$$I_g = I_{g0} \sum_j M_{gj} \delta p_j,$$

with the reference intensity I_{g0} = |A_{g0}|^2 and M_{gj} = Re[2(A_{0g})^* T_{gj}]. Clearly, the matrix M_{gj} can be inverted to yield directly the wanted (general) displacement off the reference:

$$\delta p_j = \sum_g (M_{gj})^{-1}(I_g - I_{0g}),$$

whereby for m unknown quantities δp_j the sum runs over m experimental data points I_g. However, because of experimental and computational errors involved, the direct numerical inversion has to be replaced by a minimization of the theory–experiment misfit. This is done iteratively and brings the method very near to the automated search. Of course, the method works only with parameter changes small enough to ensure the linearity δt(δp_j) ≈ δp_j. This holds exactly for stoichiometric variations of the surface as obvious from Eq. (6) and consequently the surface stoichiometry can be determined directly in the above described way. Table 1 compares directly and conventionally determined concentrations of Mo in the first three layers of the substitutionally disordered compound Mo_{75}Re_{25}(100) [36]. There is almost perfect agreement.

Application of the direct method to geometrical
displacements is more complex because $\delta t$ is a non-linear function of $\delta r$. However, for small enough displacements (typically $\delta r < 0.1 \text{ Å}$) $\delta t(\delta r)$ can be linearized, so that $\delta r$ can be determined in the direct way described. This allows the fast and effective structural refinement in real space even in case of complex structures [33–35]. The example of $(1 \times 3)$-H/Rh(110) is given in Fig. 7 where the small geometrical displacements, which hydrogen induces in the substrate, are displayed [2,37].

5. Summary

By the introduction of efficient structural search procedures and direct methods, by the perturbative and fast tensor LEED method to calculate diffraction intensities and in particular by the combination of both, LEED recently has got access to rather complex surface structures. These cover adsorbates with large unit cells with many atoms in the unit cell and complex reconstructions induced in the substrate. Beyond geometrical parameters, which can be determined with an accuracy of 0.01 Å in favourable cases, also chemical and thermal parameters as the layer dependent stoichiometry in substitutionally disordered com-

---

Table 1

Layer dependent surface stoichiometry of Mo$_{24}$Re$_{24}$(100) as determined conventionally by use of the average $r$-matrix method and directly using inverted chemical tensor LEED; the values $c_i$ represent the Mo concentration in the first three layers.

<table>
<thead>
<tr>
<th></th>
<th>Results by trial and error</th>
<th>Results by the direct method</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_1$</td>
<td>$1.00 \pm 0.14$</td>
<td>$0.97$</td>
</tr>
<tr>
<td>$c_2$</td>
<td>$0.53 \pm 0.17$</td>
<td>$0.47$</td>
</tr>
<tr>
<td>$c_{31}$</td>
<td>$0.84 \pm 0.22$</td>
<td>$0.81$</td>
</tr>
</tbody>
</table>

Fig. 6. Structural model detected by a tensor LEED based search procedure for $(3 \times 3)$-$(\text{C}_6\text{H}_6 + 2\text{CO})$/Rh(111) (after Ref. [32]).
pounds and the anisotropic vibrational amplitudes of surface atoms can be determined. This recent progress of LEED, which currently is still developing further, makes the method to remain the leading technique in surface crystallography.

References