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Direct low-energy electron-diffraction analysis of $c(2\times2)$O/Ni(100) including substrate reconstruction

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A direct low-energy electron-diffraction (LEED) method for complex adsorption structures is described as an inversion of tensor LEED and applied to the adsorption system $c(2\times2)$O/Ni(100), saving computer time by an order of magnitude. Oxygen resides in hollow sites; the first substrate layer distance is expanded and the second substrate layer reconstructs into a buckled layer. The direct method resolves the adsorption height as well as the adsorbate-induced substrate relaxation and reconstruction. The structure found compares very well to the results of a conventional analysis within the usual limits of error. Generally, the method can be expected to provide rapid access to complicated adsorption structures described by an increased number of parameters which cannot be handled in a usual trial and error procedure because of computational reasons.

In a recent publication[1] we described a new method to retrieve surface structures by low-energy electron-diffraction (LEED) intensities directly, i.e., without the usual tedious and time-consuming trial-and-error method. The trick that we played to circumvent the phase problem was taken from the "heavy-atom" technique used in x-ray crystallography. A physically reasonable guess of the surface structure (reference structure) takes the role of the heavy atom, i.e., deviations from the reference structure are treated as small perturbations. In the simplest version of the theory, intensities for a structure differing from the reference structure by small displacements δr_j of surface atoms j can be written as

$$|A_g|^2 \approx |A_{0g}|^2 + \sum_j M_{gj}\,\delta r_j \;, \tag{1}$$

where A_{0g} is the scattering amplitude of the unperturbed surface (reference surface) for a certain energy and beam labeled g. The tensor M_{gj} is the important quantity and is calculated by the recently developed method called "tensor LEED."[2,3] Obviously, as $|A_{0g}|^2$ is given by calculation of the reference structure, Eq. (1) can be inverted to yield the structural changes, and so the correct surface structure directly. Of course this might only be true when the initial reference structure and the real structure are sufficiently close. In fact, we could show that the method works for the case of multilayer relaxation of clean low-Miller-index metal surfaces for which the structural changes δr_j from the bulklike-terminated surface taken as reference structure are small, i.e., below 0.1 Å.

In this paper we report on a powerful extension of the method. We apply it for the first time to a superstructure, i.e., to $c(2\times2)$O/Ni(100). For this system, controversial results were reported in the literature. Adsorption heights between 0.85 and 0.92 Å and hollow as well as off-center adsorption sites were found including adsorbate-induced substrate layer relaxation (for a survey see Ref. 4). As the Ni(100) substrate is known to reconstruct upon adsorption of carbon or nitrogen,[5–7] adsorbate-induced substrate reconstruction may also happen which, however, in contrast to the adsorption of C and Ni, must preserve the $c(2\times2)$ symmetry. So, there is a large parameter space to scan, and the system seems to be almost ideal for application of the direct method described above.

For the reference structure we chose a bulklike-terminated substrate on which oxygen resides in the fourfold-symmetric hollow site 0.90 Å above the top layer of the substrate corresponding to an earlier analysis.[8] In order to make the calculation of the reference structure as simple as possible we started from a (1×1) adsorption structure with an oxygen atom in each hollow site. To create the reference wavefield for the $c(2\times2)$ superstructure we used a version of tensor LEED that is linear in the change of atomic scattering matrices δt rather than the displacements themselves.[2] This version holds for larger displacements, i.e., up to 0.5 Å in cases of strong scattering of the atom moved. For weaker scatterers, such as oxygen in the present case, much larger displacements are likely to be allowed. So we can use this version to remove two atoms in a (2×2) superstructure cell just by setting their scattering matrices to zero, i.e., $\delta t = -t$. In this way the wave field of the $c(2\times2)$ reference structure results and the tensor applying to Eq. (1) can be calculated. The approximation $\delta t = -t$ is a good one because multiple scattering within the oxygen layer is weak compared to substrate layers, as checked by separate calculations.

The structural parameters allowed to vary are displayed in Fig. 1. They are d_{01} and d_{12}, the spacing between the first three layers of the surface. Additionally,

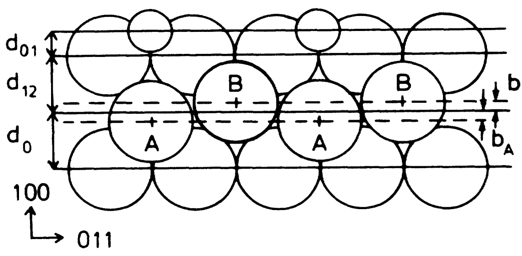

FIG. 1. Structural model for $c(2\times2)$O/Ni(100).

we allow for substrate reconstruction in the second substrate layer, which can buckle by the displacements b_A and b_B of atoms A and B, respectively, introducing a $c(2\times2)$ superstructure on their own. We want to emphasize at this point that tensor LEED allows the calculation of superstructure beam intensities even though the reference structure is unreconstructed. A reconstruction in the first substrate layer was not considered as a symmetric adsorption site was assumed and clock reconstruction introducing glide symmetry planes, as in the case of C, N/Ni(100), can be excluded from the symmetry of the diffraction pattern.

For the determination of the four parameters at least four independent data points have to be used. In the ideal case, any four data points should produce the same structure. However, in reality, measured as well as computed intensities have their error limits and produce some uncertainty for the determination of structure parameters by inversion of Eq. (1). Also, computed and experimental intensity levels can differ considerably because of surface roughness, a problem which exists in normal LEED analyses, too. It can be circumvented by proper normalization of one data set or by the use of logarithmic derivatives of intensities with respect to energy, $L=I^{-1}\partial I/\partial E$, or the related Y functions $Y=L/[1+(V_{0i}L)^2]$,[9] rather than the intensities themselves. In this paper we chose the latter procedure and used Y functions with an optical potential $V_{0i}=4$ eV. In order to reduce the influence of computational and experimental errors we applied an error minimization procedure using the following relation, where Y_g(expt) is the experimental Y function for the beam or energy g and where the Y function computed for the variables r_1,r_2,r_3,r_4 is denoted by $Y_g(r_1,r_2,r_3,r_4)$:

$$\frac{\partial}{\partial r_j}\sum_g [Y_g(\text{expt})-Y_g(r_1,r_2,r_3r_4)]^2=0\ ,\qquad j=1,2,3,4\ . \qquad (2)$$

The experimental data entering this equation were measured by Oed *et al.* and are published separately.[4] They correspond to normal incidence of the primary beam and a temperature of 120 K. Existence of $p(2\times2)$ patches was carefully avoided by controlling intensities at noncentered half-integer-order spot positions as well as by high-resolution electron-energy-loss spectroscopy, which showed no losses characteristic for the $p(2\times2)$ structure. The intensities were taken in the energy range 40–350 eV using a fast computer-controlled video system (for more details see Ref. 4). The spectra of integer-order beams (1 0, 1 1, 2 0, and 2 1) and half-integer-order beams ($\frac{1}{2}\,\frac{1}{2}$, $\frac{3}{2}\,\frac{1}{2}$) covered a total energy range of 1730 eV. With a step width of 2.5 eV this corresponds to a data basis of nearly 700 data points entering Eq. (2).

The results for the parameters d_{01}, d_{12}, b_A, and b_B are given in the first column of Table I. The values retrieved from a conventional full dynamical analysis, which is published in detail separately,[4] are displayed in the third column. Obviously, the change of parameters starting from the reference values show the correct trend, i.e., reduction of the adsorption height, substrate layer spacing expansion, and second substrate layer buckling. Also, the absolute values of the structural parameters are already close to the result of the conventional analysis. As the atomic displacements involved are considerably larger than 0.1 Å, which is the limit of validity of the linear version of tensor LEED,[1] we took the structure found as a new reference structure (except for $b_A=b_B=0$) and repeated the determination of the structure parameters and the minimization procedure as described above. The results are given in the second column of Table I. Obviously all structural parameters now compare even better to the parameters of the conventional analysis. The latter gives a best-fit Pendry R factor of $R=0.28$ as averaged over the set of six beams and the total energy range of 1730 eV.[4] The discrepancies between the present directly and the conventionally determined structural parameters are not larger than a few hundredths of an angstrom, i.e., of the order of the

TABLE I. Results of the direct LEED method for $c(2\times2)$O/Ni(100) compared to results of the conventional LEED analysis (Ref. 4).

Structure parameters	Reference structure 1 $d_{01}=0.90$ Å $d_{12}=1.76$ Å	Reference structure 2 $d_{01}=0.72$ Å $d_{12}=1.89$ Å	Conventional analysis (Ref. 4)
d_{01} (Å)	0.72	0.73	0.77
d_{12} (Å)	1.89	1.87	1.86
b_A (Å)	−0.02	−0.02	−0.02
b_B (Å)	+0.00	+0.01	+0.02

usual error limits of LEED analyses or even smaller.

So, the version of direct methods based on tensor LEED linear in displacements works even in the case of adsorbates including induced substrate relaxation and reconstruction. The structural parameters are correctly reproduced within the error limits typical for LEED. It seems that the direct method, even in its present simple form, provides a powerful tool to resolve even complex structures. We want to emphasize that the choice of the reference structures does not seem to be critical as long as it is not too far away from the correct structure. So we could have started from any physically reasonable structure without knowing the result of the preliminary analysis.[8] In the present case an order of magnitude of computer time was saved compared to the traditional trial and error method. In more complex cases, where the conventional analysis may not allow us to vary a correspondingly large number of parameters because of computational reasons, the method can be expected to give an idea of the adsorbate-induced movements of the various substrate atoms possibly extending into deeper layers. For control a structural refinement through final full dynamical calculations around the structure found could follow.

For the particular system $c(2\times2)$O/Ni(100) it turns out that consideration of substrate relaxation and reconstruction is essential, which so far had not been systematically varied to yield the correct structure. The adsorption height is much lower than obtained by earlier analyses and the expansion of the top substrate layer spacing is as much as $+6\%$ of the bulk value. Though the buckling reconstruction is weak, it undoubtedly is there as demonstrated by a considerable improvement of fractional-order spot spectra.[4] In the conventional analysis[4] off-center adsorption sites of oxygen could be ruled out, but the present linear version of the direct method cannot handle them: the resulting domain structure of symmetrical displacements cancels in the linear approximation. However, higher-order versions such as described in Ref. 1 will handle such complications, returning a probability distribution over sites.

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