Surface structure determination via a transform-deconvolution method

Uzi Landman and D. L. Adams

Xerox Corporation, Rochester Research Center, Webster, New York 14580
(Received 8 August 1973)

A fast direct-transform method for the determination of surface structures from low-energy-electron diffraction (LEED) intensity data is presented. Basic principles of a proper transform construction and its applications are discussed and demonstrated. The effects of data truncation is studied and a deconvolution procedure for extraction of accurate structural information from the transform is described. Results of a complete surface structure determination of Ni(100) by application of the method to experimental data are discussed.

I. INTRODUCTION

Basic to studies of physical processes occurring on solid surfaces is the understanding of the geometric and electronic structure of the outermost few atomic layers of the solid. Of particular importance is the geometrical structural information since it is an elementary essential for the construction of physical models of surface phenomena. Determination of surface structures from low-energy-electron diffraction (LEED) experiments requires analysis of the angular distribution and intensities of diffracted beams (diffraction patterns and intensity-voltage profiles). The customary analysis of LEED intensity measurements consists of attempts to fit experimental data via model calculations. The high degree of uncertainty in the results derived by the above methods originates from an incomplete description of the physical phenomena associated with the diffraction of low-energy electrons and in the unavoidable failure to test all the possible structures of the system.

The technique presented in this paper consists of direct transform analysis of experimental data which avoids to a large extent the above uncertainties along with a significant reduction in computational time and storage. In order to demonstrate the principles and applications of our transform method for surface structure determination, we employ intensities calculated on the basis of kinematical diffraction, application of the transform method to the analysis of real data is also included.

The construction and characteristics of the transform method applied to LEED with particular reference to the finite extent of the data, and physical interpretation, are discussed in Sec. II. In Sec. III we present structural determination of the (100) face of Ni, based on transform analysis of the experimental data of Demuth and Rhodin.

II. DIRECT TRANSFORM TECHNIQUE

A. Transform Construction

As an introduction to the formulation of the direct transform method for LEED it is instructive to briefly review the construction of the Patterson function used in x-ray structure analysis, which is defined as

\[ P(x,y,z) = \frac{1}{V} \sum_{h,k,l} I_{hkl} \exp[2\pi i(hx + ky + lz)], \] (1)

where \( I_{hkl} \) is the intensity of the \((hkl)\) diffracted beam, and \( V \) is the volume of the sample. Due to the kinematical elastic nature of x-ray diffraction (in the absence of anomalous dispersion) it follows that the Patterson function \( P(R) \) can be expressed as the autocorrelation of charge densities

\[ P(R) = \int \rho(\mathbf{r})\rho(\mathbf{r}+\mathbf{R})d^3r. \] (2)

The expression in Eq. (1) can be further simplified (in the absence of anomalous dispersion) through the application of Friedel's law yielding a real cosine transform of the diffracted intensities rather than the complex exponential transformation in Eq. (1).

In constructing a transform appropriate for surface structure analysis, the nature of the LEED process dictates certain modifications to the Patterson function as used in x-ray studies. Characteristic to low-energy-electron diffraction is the dynamical nature of the scattering process and the inelastic collision damping of the electron-beam propagation in the direction normal to the surface. Since momentum is conserved in the plane parallel to the surface but not in the normal direction, the diffracted intensities are characterized by discrete \((hkl)\) Miller indices of the surface net and the continuous variable \( S \), the momentum transfer in the normal direction. This variable is constrained to positive values due to the half space nature of low-energy-electron diffraction measurements in which only back-scattered electrons are detected.

These considerations lead us to the following formulation of the transform

\[ P^u(x,y,z) = \sum_{h,k} \int_0^\infty ds I_{hks}(S) \times \exp[2\pi i(xh + ky)] \exp[2\pi iSz]. \] (3)
B. Use of Projections and Sections in Structure Determination

The transformation given in Eq. (1) defines a three-dimensional vector space. Each point \((x,y,z)\) in this space represents a position vector \(\mathbf{R} = (x,y,z)\) connecting two scattering centers, translated to an arbitrary common origin. In most cases that we have studied, structure determination can be based on the analysis of projections and sections of the transform rather than the full three-dimensional function. Of particular use in surface structure analysis is the one-dimensional projection of the transform in Eq. (3), denoted by \(P_M(z)\)

\[
P_M(z) = \int_0^\infty dSI_00(S) \exp[2\pi i S z],
\]

where \(I_0\) is the intensity of the specularly diffracted electron beam. This projection is used in the determination of layer spacings as demonstrated below. Determination of layer registry is achieved by the analysis of sections of the \(P_M\) transform, denoted by \(P_M(x,y,p)\), where \(p\) specifies the level in the normal direction in which the section is made. To demonstrate the use of projection and sections, we consider a \((2 \times 2)\) overlayer model system with an overlayer-substrate spacing of \(d_s/2\), where \(d_s\) is the spacing between consecutive substrate layers. Using for illustrative purposes a \(s\)-wave scattering model with scattering phase shifts \(\delta_s = \pi/2\) and \(\delta_1 = \pi/8\) for the substrate and overlayer ion-cores, respectively, yields the kinematical intensity profiles of the \((00)\) beam shown in Figs. 1(a) and 1(b) for the clean substrate (dashed) and overlayer system (solid). We note that for this configuration no new peaks occur (in the absence of multiple scattering), the profiles being different in line shape and relative intensities only.

In the following, we use the line projection \(P_M(z)\), [Eq. (4)] which contains the projections of the interatomic vectors on the \(z\) axis, and the two-dimensional section \(P(x,y,p)\) which contains the interatomic vectors between atoms at \((x,y,z)\) and \((x,y,z)\) where \(p = z_1 - z_2\), projected on the \((xy)\) plane. The real part and modulus of the projection \([\text{see e.g. Eq. (4)]}\) obtained by transforming the above overlayer intensity profile are shown in Figs. 1(d) and 1(f), respectively, while these for the clean surface are shown in Figs. 1(c) and 1(e). The expected locations of peaks are denoted by vertical arrows. It is seen that in both modes of the projection, peaks occur at \(z = n(d_s/2)\) \((n = 0, 1, 2, \ldots)\) in the overlayer case, whereas in the transformation of the intensity profiles of the substrate, the maxima at odd values of \(n\) are missing, as expected. Attention is drawn to other peaks in the projection which are not associated with atomic locations in the model structure.

Unlike the x-ray case, this transform does not reduce to a real cosine transform since Friedel's law is not obeyed due to inelastic collision damping. (In recent publication, Clarke et al. used a real cosine transform for the analysis of LEED data. We emphasize the lack of a priori justification for this procedure for surface structure analysis. In addition, these authors fail to treat the problem of data truncation which we discuss further in Sec. C.)

J. Vac. Sci. Technol., Vol. 11, No. 1, Jan./Feb. 1974
sections of the transform is demonstrated in Fig. 2. Sections at the level \( n = d_s/2 \), \([P(x,y,0)]\), for the two-fold and four-fold registries are shown in Figs. 2(a) and 2(c), respectively, along with the \( z = 0 \) section \([P(x,y,0)]\) in Fig. 2(b). These sections were derived from the specular and non specular diffracted beams \((h, k = 0, 1, 2\), indexed according to the substrate reciprocal net\). The \( P(x,y,0) \) sections are essentially the same for both overlay registries since this section contains projections of interatomic vectors between atoms located in the same \((xy)\) plane (i.e., \( z \) level), whereas the \( P(x,y,p) \) sections reflect different interlayer registries.

C. The Problem of Data Truncation

The extent and range of data is commonly a critical factor in the analysis of sampled experimental measurements. The particular problem in the application of transform methods to the analysis of LEED data is the finite number of diffraction beams and the finite range of their intensity profiles measured in the conventional LEED experiment. Since we have found empirically that reliable \((xy)\) sections of the transform can be obtained using a rather small number of non specular diffraction beams [see e.g., discussion in the next section where the intensity profiles of the specular and three non specular measured diffraction beams are employed in deriving two-dimensional transform sections for the \((100)\) face of Ni], we confine our discussion at this time to the effects of the finite range of the \((00)\) beam intensity profiles on the transform analysis.

We define an ideal intensity profile for the application of our transform analysis, as shown in Fig. 3(a). This profile represents the contribution of the interference function including damping, to the kinematical intensity, i.e., the intensity of low-energy electrons diffracting kinematically from an ordered array of ion-core unit scatterers. This ideal intensity profile is periodic with peaks of constant amplitude, and extends to an infinite value of the normal momentum transfer variable. The \( P^M(z) \) transform associated with the above profile is shown in Fig. 3(A) and consists of a periodic series of delta functions at positions corresponding to the projections on the \( z \) axis of all vectors between the ion-core unit scatterers.

Operationally a typical LEED measurement may be considered as viewing the above profile [Fig. 3(a)] through a data-window which affects the range and line shape of the record. Two possible data-windows are shown in Fig. 3(b). The window denoted by \( \omega_1 \) is a box-car window which merely confines the range of the record, whereas the \( \omega_2 \) window both limits the range of the record and also affects its line shape. This second window transforms the “ideal” interference function signal in Fig. 3(a) into the “realistic” profile shown in Fig. 3(c2). The truncation effect of the \( \omega_2 \) window on the ideal signal is illustrated in Fig. 3(c1), where the ideal record [Fig. 3(a)] is terminated at some finite value \( S_M \) of the normal momentum transfer. The effect of multiplying the ideal intensity profile by the data windows, upon the transform of the products is shown in Figs. 3(C1) and 3(C2), where the modulus of the \( P^M(z) \) projection for both profiles is given. Comparison of these results with the transform associated with the ideal signal [Fig. 3(A)] indicates that “windowing” the ideal profile results in a broadening of the delta functions and in the occurrence of additional peaks in the transform (Gibbs oscillations), which are not directly related to the geometry of the array of ion-core scatterers.

From the above discussion, it is evident that a central problem in the extraction of structural information from transforms of LEED intensity profiles is the need to differentiate between peaks in the transform arising from the structural arrangement of the scattering centers and those arising from data truncation.
to precisely locate the “true” peaks. The solution to this problem arises from a consideration of the effects of data windows in real space, rather than as above in momentum space. This is achieved through application of the Convolution Theorem,\textsuperscript{18} which may be written as

\[ F[g \ast h] = G \ast H, \]

where \( g \) and \( h \) are arbitrary functions, \( G \) and \( H \) are the transforms of \( g \) and \( h \), respectively, \( F \) represents the Fourier transform operation, and “\( \ast \)” denotes the convolution operation. Thus, in the present context the transform of the multiplication of the ideal intensity profile [Fig. 3(a)] by a data window [Fig. 3(b)], \( P^M_{\text{OBS}}(z) \) [Figs. 3(C1)–3(C2)], is equivalent to a convolution in real space of the transform of the ideal profile, \( P^M_{\text{DEL}}(z) \) and the spectral window, \( W \), i.e.,

\[ P^M_{\text{OBS}}(z) = P^M_{\text{DEL}}(z) \ast W(z). \]

This point is illustrated in Fig. 3; convolution of the transforms, \( W_1 \) and \( W_2 \) [Figs. 3(B1) and 3(B2)] of the data windows \( \omega_1 \) and \( \omega_2 \), with the transform, \( P^M_{\text{DEL}}(z) \) [Fig. 3(A)], of the ideal profile yields the transform functions shown in Figs. 3(C1) and 3(C2), respectively.

Since by the convolution theorem \( P^M_{\text{OBS}}(z) \) in Eq. (6) is simply the transform of the \textit{finite} intensity profile, the equation can be solved for \( P^M_{\text{DEL}}(z) \), if the data window \( \omega \), and hence its transform \( W \), is known. Accordingly, we have constructed a transform-deconvolution procedure\textsuperscript{18} which proceeds in the following steps.

1. The transform of the intensity data is performed.
2. A trial delta function transform is constructed and its convolution with the appropriate spectral data window is calculated.
3. The fit between the observed transform obtained from step 1 and the calculated transform resulting from step 2 is determined.
4. Steps 2–3 are iterated until a best fit is obtained.

The final value of the delta function transform distinguishes the “true” peaks in the observed transform and their positions to a high degree of precision, as is demonstrated in the analysis of LEED intensity data from Ni(100) in the following section.

It is interesting to note at this point that an alternative method of suppressing the effects of data truncation has been suggested.\textsuperscript{18} This consists of a multiplication in momentum space of the intensity profiles by a data window chosen to minimize the Gibbs oscillations in the transform. We have found that this procedure, using an appropriate window function,\textsuperscript{19} can significantly attenuate the data truncation peaks, but only at the expense of a very considerable, and for our purposes, unacceptable loss of resolution in the transform. This effect can be readily understood by noting that the equivalent procedure in real space, by the convolution theorem, consists of a convolution of the transform of the data window with the transform of the intensity profile. In practice the spectral window (transform of the data-window) is chosen to minimize the side lobes of the function, in order to reduce the Gibbs oscillations, but this has as corollary the effect of broadening the main lobe, and consequently of further broadening the peaks in the transform of the intensity profile.

\section*{D. Geometrical Interpretation of the Transform}

As we have noted in an earlier section, in the case of x-ray diffraction, the Patterson function [Eqs. (1) and (2)] represents the self-convolution of charge densities in the diffracting material, and is in principle a real, positive definite function. The transform that we have constructed for the LEED case [Eq. (3)] is a complex function. The main characteristics of LEED intensity profiles consist of peaks at positions corresponding to the satisfaction of the basic laws of diffraction, dressed by the effects of multiple scattering and details of the

\[ J. \text{Vac. Sci. Technol., Vol. 11, No. 1, Jan./Feb. 1974} \]
scattering potential. It can be shown easily that the square of the modulus of our transform is equal to the transform of the autocovariance function of the intensity profile,

\[ |P^M(z)|^2 = \int dSC(S) \exp[2\pi iSz], \]  

(6)

where \( C \) is the autocovariance function defined as

\[ C(\tau) = \int dSI_0(S)I_0(S+\tau). \]  

(7)

By construction, the autocovariance of the intensity profile seeks and enhances periodic features in the intensity profile, and in addition, performs a local averaging in momentum space. Thus, the main maxima in the transform of the autocovariance function are associated with the above mentioned periodicities in the intensity profile dictated by the diffraction laws and the geometrical arrangement of the scatterers.

III. APPLICATION TO SURFACE STRUCTURAL DETERMINATION OF Ni(100)

Having discussed some principles of our transform method, we present in this section an application of the technique to the LEED data obtained by Demuth and Rhodin\(^4\) for Ni(100). The intensity profiles for the specularly diffracted beam for various angles of incidence are shown in Fig. 4(b). These profiles exhibit strong dynamical characteristics and extend over a range of \( \sim 10-240 \) eV.

The transform projections obtained from the above profiles, together with the transform result for the angle averaged intensity curve are shown in Fig. 4(a). We note that for this system there is no marked improvement achieved in the real part of the transform by angular averaging. The resulting values for the layer spacing based on the individual profiles are in the range of \( 1.76-1.81 \) Å, in excellent agreement with the x-ray bulk value of 1.76 Å. As an illustration of the use of the deconvolution procedure, we include also in Fig. 4(a) the convoluted-delta-function best fit to the transform of the \( \theta=12^\circ \) intensity profile. The best-fit result for the layer spacing is 1.78 Å as compared to a peak in the transform of the \( \theta=12^\circ \) profile at 1.80 Å.

A complete determination of the structure was achieved by calculating two-dimensional sections of the transform, using the above specular diffraction profiles and the intensity data for the (01), (10), and (11) diffracted beams which were measured\(^4\) for an azimuthal angle \( \psi = 0^\circ \), and polar angles of incidence \( \theta = 0^\circ \) for the (10) and (11) beams, and \( \theta = 2^\circ \) to \( 2^\circ \) (in steps of \( 1^\circ \)) for the (01) beam. The resulting sections are shown in Figs. 4(c) and 4(d) for the levels \( \rho = 0 \) Å, \( [P^M(x,y,0)] \), and \( \rho = 1.78 \) Å, \( [P^M(x,y,1.78 \text{ Å})] \), respectively. These sections exhibit the expected characteristics of the interlayer and intralayer registry in the (100) plane and enable the determination of the lateral and vertical location of atoms in the surface layers to an accuracy of better than 5%.

IV. SYNOPSIS

In conclusion, we have outlined in this paper the principles of our transform-deconvolution method for the determination of surface structures from LEED data. We have demonstrated the application of the
method to the complete determination of the surface structure of Ni(100) from experimental data. The method is currently being used for the determination of the atomic arrangements in both clean and overlayer systems.15

ACKNOWLEDGMENTS

The authors are indebted to the staff of the Sigma-7, Rochester Technical Computer Center, in particular Donald D. Smith and Richard R. Bergan, and to John E. Klock and Paul R. Pellika of the Art Services for their invaluable cooperation and help. Mrs. Carol Troy is gratefully acknowledged for her assistance in the preparation of the manuscript.

4 J. E. Demuth and T. N. Rhodin (to be published).
9 Multiple-scattering features in the intensity profiles do not alter the characteristics of our transform deconvolution technique and its general method of application. Analysis of the experimental intensity data for Ni(100) proved to be successful despite the marked dynamical structure of the measured intensity profiles (see e.g., Sec. III). This conclusion derives in part from the smoothing characteristics of the autocovariance function (see Sec. IID). In some cases it might be advantageous to use angular averages of the diffracted beams, including in the averaging a rather small number of intensity profiles which span a wide range of incidence angles. Details of this study will be reported elsewhere (U. Landman and D. L. Adams, to be published).
11 Alternative methods of deconvolution using Laplace transformation and matrix inversion are under study.
12 M. G. Legally (private communication).
15 D. L. Adams and U. Landman (to be published).