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Real-Space Multiple Scattering Theory Calculations of LEED Intensities for Stepped Surfaces

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Abstract

We use a newly developed real-space multiple scattering theory (RS-MST) to calculate low-energy electron diffraction (LEED) intensities from stepped surfaces. In this calculation the electron wavefunctions are expanded in terms of an angular momentum basis, utilizing the property of removal invariance of systems with semi-infinite periodicity. This strongly reduces the dependence of the calculation on the interlayer spacing and thus opens up the possibility of treating more open surfaces. This includes in particular stepped surfaces, to which conventional methods cannot be applied. Applications of the formalism to various stepped surfaces are presented. In particular, the results for Cu(311) and (331) surfaces obtained from both the layer doubling and RS-MST methods are compared. In addition, numerical techniques which can improve the convergence as well as the speed of the RS-MST approach are discussed.

1. Introduction

It is known that stepped surfaces are important in studying the properties of many materials and understanding processes in many technologies. For example, steps can provide active sites for bond breaking and bond formation in heterogeneous catalysis. They can also affect the mechanical properties of solids through the pinning of dislocations and crack propagation. In order to understand these phenomena, it is often necessary to obtain accurate information about atomic positions on the steps of a surface.

Quantitative determination of the structures of clean stepped surfaces has been difficult. Conventional theoretical techniques for the study of LEED spectra cannot be readily applied to stepped surfaces. This is due to the small interplanar spacing and large two-dimensional (2-d) unit cell of a stepped surface, which causes difficulties with the convergence of the plane wave expansion used in a conventional LEED theory.

However, a recently developed technique [1-3] has greatly alleviated this problem. This technique is based on a real-space formulation of multiple scattering theory (RS-MST) [1] and dispenses completely with plane waves (except of course in the trivial propagation through vacuum from the electron gun to the surface and back to the

detector). Within the surface, it only uses spherical waves and strongly reduces the scaling problems of the plane wave basis used by the earlier methods [4,5]. RS-MST is based on the principle of removal invariance which holds for semi-infinite periodic lattices: removing a layer from the free end of such a lattice does not change the electronic states (except for a trivial phase factor), because the resulting surface is identical to the original one, being merely displaced with respect to that by a single layer. This removal invariance provides a self-consistency condition for the electronic states, which can be solved numerically. Detailed discussion of this new approach and RS-MST can be found in references [1-3]. In this paper we will focus on the application of the method to several stepped surfaces of Cu.

2. Theory

We first consider the ideal bulk termination of the crystal. In general, however, the selvedge will undergo some form of restructuring, exhibiting planar relaxation perpendicular and/or parallel to the surface and perhaps reconstruction of the first few atomic layers, and may also involve adsorbates. Such deviations from the ideal semi-infinite bulk lattice can be readily incorporated and will be discussed later in this section.

The bulk termination of an ideal crystal exhibits a universal property, a consequence of the semi-infinite periodicity perpendicular to the surface. In simplest terms it implies that the reflectivity of the crystal is unchanged if an atomic plane is peeled away from the surface. More generally, we can say that the full scattering t-matrix of the system is invariant with respect to the removal of any finite number of layers from the surface. This *removal invariance* property is the foundation of our new approach to LEED theory. It allows us to derive an equation within a purely angular momentum basis to determine the t-matrix corresponding to a semi-infinite periodic system, which in turn can be used to evaluate the reflectivity of the entire surface.

Instead of using a layer doubling approach as in the plane-wave representation, in the angular momentum representation we use a self-consistency condition to determine the reflectivity of the half solid. To do this we use the property of removal invariance in the presence of semi-infinite periodicity [1]. We imagine replacing the half solid with a single *renormalized* layer which is constructed in such a way as to possess the scattering properties of the entire half solid. This renormalized layer is described by a t-matrix, $\mathcal{T}$, in angular momentum representation. According to the property of removal invariance, a system consisting of a bare atomic layer, represented by the monolayer t-matrix, τ_{lay}, and a renormalized layer, $\mathcal{T}$, can also be represented by the t-matrix, $\mathcal{T}$. This constitutes a self-consistency condition from which $\mathcal{T}$ can be determined. In practice, a more rapidly convergent procedure is to consider a half-solid being represented by a stack of N layers, properly renormalized to reproduce all the scattering properties of the half-solid. The self-consistency condition can be constructed by adding one more layer, represented by τ_{lay}, and demanding that the resulting system can still represented by $\mathcal{T}$. We call such a procedure an N-layer calculation, or $(1, N)$ mode.

It can be shown that the solution of the self-consistent equation, as formulated in Ref.[3], takes exact account of all multiple scattering paths within any $N+1$ nearest neighbor layers. All multiple scattering terms between layers further apart are represented by the products of Green's functions and translation operators, which involve

internal summations over angular momentum states that are truncated at a finite l. This consideration provides a basis upon which one can estimate the rate of convergence in terms of the angular momentum truncation and make a proper choice of the value of N in a calculation. Specifically, N should scale roughly by Nd =const., where d is the interplanar spacing of the system. Therefore, the size of the basis set for a RS-MST calculation scales as $1/d$, compared with that of a plane wave basis set which scales as $1/d^3$ [3].

The above discussion applies to an ideally truncated unrelaxed surface. A more realistic model of a surface usually includes several relaxed layers and sometimes adsorbates. The use of the angular momentum representation provides an easy multiple scattering approach for the treatment of surface relaxations and adsorbates. Once the t-matrix, $\mathcal{T}$, of the unrelaxed substrate is known, one can use multiple scattering theory to construct the t-matrix, $\mathcal{T}_{relax}$, for the relaxed surface by combining the t-matrix, $\tau_{overlay}$, of an overlayer with $\mathcal{T}$ of the substrate. This process can be used repeatedly for relaxations and adsorbates involving more than one layer.

3. Results

In this section we present LEED I–V spectra for Cu fcc surfaces obtained with the new RS-MST for several surface structures. First we compare the I-V spectra for unrelaxed surfaces with that obtained by the layer doubling technique. In all calculations the atomic Cu phase shifts are obtained from solving the Schrödinger equation for the potential provided by Moruzzi, Janak and Williams [6]. We found that six atomic phase shifts ($l_{max} = 5$) were sufficient for energies below 80eV, and $l_{max} = 6$ was required from 80eV to 200eV. We used a three-layer calculation ($N = 3$ in the self-consistent equation, see Ref.[3]) for the (311) surface, a four-layer calculation ($N = 4$) for the (331) surface, and a six-layer mode ($N = 6$) for the (321) surface when $E < 55$eV, a seven-layer mode ($N = 7$) when $E \geq 55$eV. All calculations are for normal incidence.

Figure 1 shows I–V curves for (10) and ($\bar{1}0$) LEED beams calculated for a Cu(311) surface using both a conventional layer doubling technique and the real-space multiple scattering theory method. This system has an interplanar spacing of about 1.09Å. The comparison between the RS-MST results (solid curves) and those obtained from the layer doubling calculation (dashed curves) are in good agreement. We found that both the numerical stability and the converged solution of the self-consistent equation are sensitive to the accuracy of the Green functions (structure constants) at high energies. In Fig. 2, we present similar I-V curves for the Cu(331) surface, which has an interplanar spacing of 0.83Å. In this case, the layer doubling method (dashed curves) begins to show signs of failure. We see that the I-V curves obtained by layer doubling shows sharp spikes at about $E \approx 120$eV, indicating convergence problems.

Finally, in Fig. 3 we show the I-V curves of Cu (321) surface, with an interplanar spacing 0.48Å, obtained by RS-MST, and for three different top layer positions relative to the bulk truncation, -5%, 0, 5%, respectively. We included in the calculation the temperature effects corresponding to $T = 300$K. The rather small change in the I-V curves with respect to the surface relaxation reflects that a 5% change in d represents a much smaller change in the lattice position when d is small.

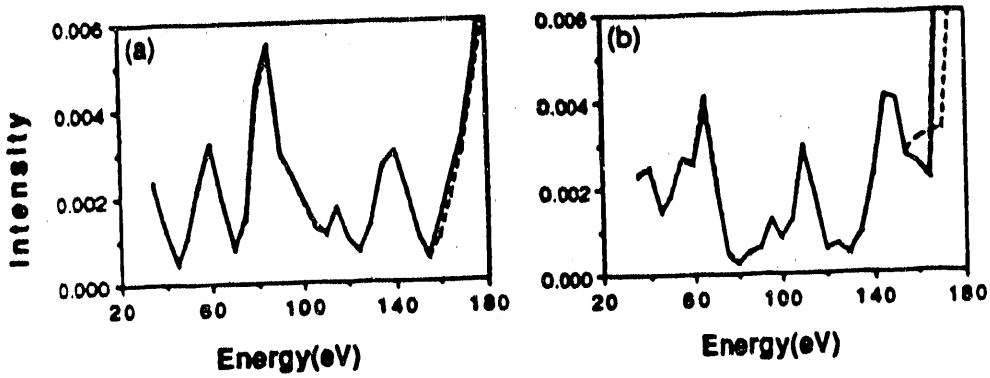

Fig. 1. The comparison of the I-V curves obtained by the RS-MST method (solid curves) and the layer doubling method (dashed curves) for Cu (311) unrelaxed surface, (a), (10) beam, and (b), ($\bar{1}0$) beam.

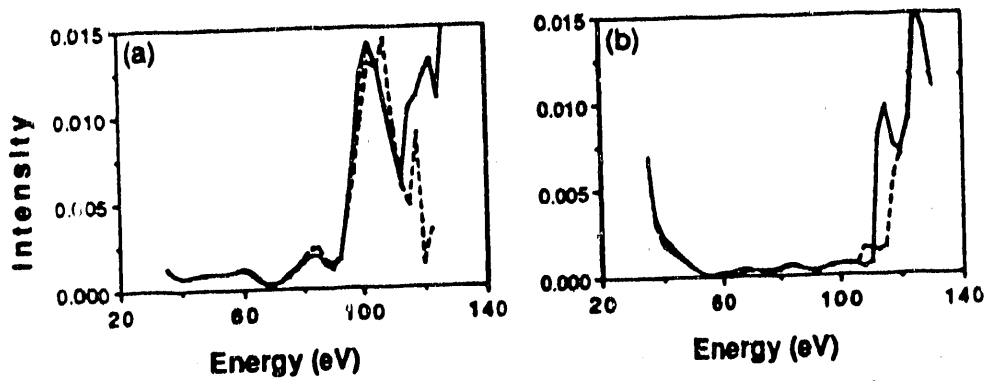

Fig. 2. Similar comparison as in Fig. 1 for Cu (331) unrelaxed surface, (a), (10) beam, and (b), ($\bar{1}0$) beam.

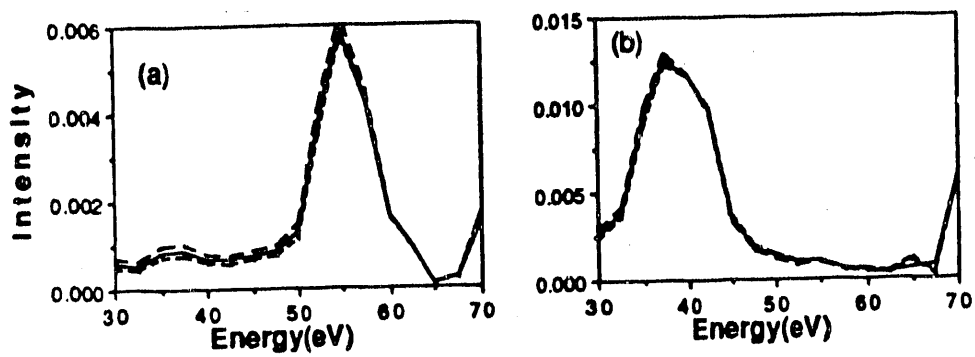

Fig. 3. I-V curves obtained by RS-MST for Cu (321) surface with three different top layer positions, -5% (broken lines), 0% (solid lines), 5% (dashed lines), relative to the bulk truncation, (a), (20) beam, and (b), ($\bar{1}\bar{1}$) beam.

4. Discussion

We have applied the RS-MST method for the calculation of LEED I-V curves of stepped surfaces. The technique is based on equations expressed entirely in terms of matrices in the angular momentum representation. The technique, unlike conventional LEED theory, is equally applicable to both low and high Miller index surfaces since the increase of the matrix size associated with decreasing interplanar spacing is much more modest than in conventional LEED calculations. It has clear advantages in treating high-Miller index surfaces. The new method has been tested on Cu (311) and (331) stepped surfaces where excellent agreement with the layer doubling method was obtained, where latter converges. The I-V curves for Cu (321) surface were calculated for the first time with the new method. This calculation demonstrates the ability of the RS-MST method to deal with high Miller-index surfaces and to treat surface relaxations with relative ease.

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5. References

[1] X.-G. Zhang and A. Gonis, Phys. Rev. Letters 62, 1161 (1989).
[2] J.M. MacLaren, X.-G. Zhang and A. Gonis, Phys. Rev. B40, 9955 (1989).
[3] X.-G. Zhang, P.J. Rous, J.M. MacLaren, A. Gonis, M.A. Van Hove and G.A. Somorjai, Surf. Sci., in press.
[4] J.B. Pendry, **Low Energy Electron Diffraction**, (Academic Press, London, 1974).
[5] M.A. Van Hove, W.H. Weinberg and C.-M. Chan, **Low-Energy Electron Diffraction: Experiment, Theory and Surface Structure Determination** (Springer-Verlag, Heidelberg, 1986).
[6] V.L. Moruzzi, J.F. Janak and A.R. Williams, **Calculated Electronic Properties of Metals** (Pergamon, New York, 1978).

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