PHYSICAL REVIEW B VOLUME 20, NUMBER 6 15 SEPTEMBER 1979

Multiple scattering of conduction electrons at disordered metal surfaces

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(Received 20 March 1979)

A conduction-electron probability of specular reflection and higher-order diffraction from an atomically smooth but contaminated metal surface is calculated for the full range of surface disorder. The average-t-matrix approximation is used to obtain the average surface-scattered-electron wave function and current density. The effects of multiple scattering between adsorbed impurities and of evanescent waves at the surface are especially considered. A resonance, in the conduction-electron probability of specular reflection from the surface, that is associated with both multiple scattering and the presence of a diffracted wave is found. The multiple-scattering theory is shown to predict minimum diffuse conduction-electron scattering at full coverage of adsorbate and maximum diffuse scattering at half coverage of adsorbate in agreement with experiment and in contradistinction to a single-scattering theory.

I. INTRODUCTION

There is a considerable body of experimental literature related to the manner in which adsorbed impurities scatter conduction electrons at a metal surface, especially in the context of the effect of adsorption on electrical and magnetic properties of metal films.[1,2] Little theoretical effort, however, has been directed towards this particular problem, although a fair amount of theoretical work has been developed for the associated problem of scattering from rough surfaces.[3,4]

Greene and co-workers, in two fundamental papers,[5,6] have treated conduction-electron scattering by contaminated semiconductor surfaces. Many authors have recently incorporated these theories in their own theoretical[7-9] or experimental[10-13] work. As pointed out by Greene,[6] however, the Greene theories do not treat the important consideration of multiple scattering between adsorbed impurities nor do they give a full account of interference effects between emerging surface-scattered waves. Their treatment of the scattering problem has also been conducted in lowest order (Born approximation) which is not a favorable approximation for low-energy conduction-electron scattering from nonweak surface perturbations at a metal surface.

In the present work, we therefore consider the way in which smooth contaminated metal surfaces may be expected to scatter conduction electrons — with particular attention to the effects of multiple scattering and interference between propagating and nonpropagating (evanescent) waves at the surface. To make the problem tractable we examine the scattering problem in the context of scattering from highly localized scattering centers, which we take to be a reasonable first approximation for impurities adsorbed onto metal surfaces, where screening is most effective, and superior to the Born approximation.

In Sec. II, we give the basic assumptions of our model and review a theory (discussed in a previous paper by More and the author) for scattering by a single impurity adsorbed onto a metal surface. We then generalize this theory to scattering by a high random coverage of adsorbate. A technique, the average-t- matrix approximation, borrowed from bulk alloy theory, is adapted for this purpose. This approach consists of approximating, in terms of averaged scattering properties, an actual disordered (contaminated) surface by an ordered configuration of fictitious or "coherent" potential superimposed over the clean-state potential.

Section III presents the calculations necessary to find the scattering amplitudes expected to arise from a contaminated surface, here represented, on the average, by a grid of coherent complex potential. The scattering amplitudes are exhibited as reflection coefficients for various diffracted beams that arise as constructive superpositions from the multiple-scattering theory. These beams occur over a background of random scatterings. The equations describing them illustrate their dependence on a number of pertinent parameters. These include the angle of incidence of the conduction electron upon the surface; the conduction-electron wavelength which in our model is a measure of the Fermi energy of the metal; the work function and the lattice parameters at the surface; the scattering strength of the adsorbate atom in the nonadsorbed state (i.e., imagined to be positioned in the bulk); and the adsorbate concentration on the surface.

Sections IV, V, and VI are devoted to a presentation and discussion of the results. We obtain a more complex behavior for scattering amplitudes than suggested by previous authors. In particular, we find a *resonance* effect in the conduction-electron probability of specular reflection. We also compare the multiple-scattering calculation with a single-scattering calculation (which ignores multiple scattering between adsorbed impurities but includes multiple scattering between the unperturbed surface potential and a single adsorbed impurity). As expected, the two theories are in close agreement for low adsorbate concentrations. They are, however, in serious disagreement for higher concentrations. Specifically, the single-scattering theory fails to predict the reasonance effect and also fails to describe the conduction electron's expected scattering properties as the surface contamination approaches full monolayer coverage. Finally, we show the necessity of a multiple-scattering theory to explain a maximum, at half coverage of adsorbate, in the conduction-electron probability of diffuse surface scattering and we relate this property to some pertinent experiments.

II. BASIC ASSUMPTIONS AND THEORY

A. Preliminaries

As in the Greene theories, we consider the most fundamental case of scattering of free electrons from a surface with a random coverage of adsorbed impurity atoms. Since we are primarily interested in deducing the theoretical implications of a complete treatment of multiple scattering and interference phenomena on surface scattering, a free-electron approximation seems appropriate as an initial excursion into this problem. We also assume a nonreconstructed metal surface. This, in fact, is a common situation for many metals at low temperatures[14] (ignoring relaxation of the surface atoms).

We represent the clean-state surface potential by a step function in the x direction with the step, V_0, constructed at the surface plane ($x=0$) and equal to the sum of the Fermi energy and the work function of the metal. The electron wave function for the clean state is then simply

$$\phi_{\vec{k}}(\vec{r}) = \begin{cases} 2ie^{i\delta}\sin(k_x x - \delta)e^{i\vec{k}_\parallel\cdot\vec{r}}, & x \leqslant 0\ , \\ Te^{-K_x x}e^{i\vec{k}_\parallel\cdot\vec{r}}, & x \geqslant 0\ . \end{cases} \tag{1}$$

Here $\hbar k = \hbar(k_x, \vec{k}_\parallel)$ is the crystal momentum quantum number identifying the electron wave function; $K_x^2 \equiv 2mV_0/\hbar^2 - k_x^2$; and the boundary condition at the interface trivially yields $\tan\delta = k_x/K_x$.

This surface model potential is commonly used in describing other surface-related phenomena[14] (e.g., electron field emission) and is expected to reasonably approximate the actual situation of scattering from a potential barrier that varies smoothly (over essentially an interatomic distance) at the surface. It is clearly an improvement over the infinite step model used in the previous theories.[5,6]

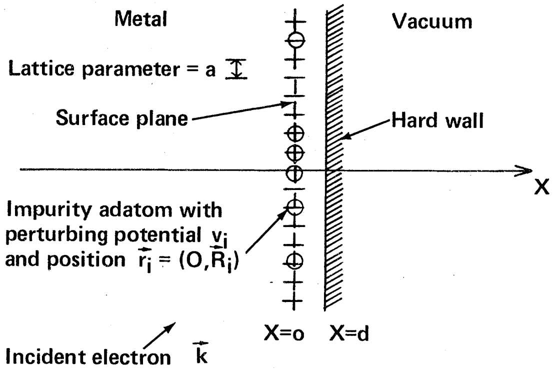

FIG. 1. Remodeled scattering at a contaminated surface.

It is most useful, however, to avail oneself of the mathematical simplicity that arises in infinite step, or "hard wall", scattering. This is accomplished by replacing the finite step at the surface by an infinite step constructed a certain distance, d, away from the surface and into the vacuum.[15] The distance, d, at which the hard wall is located must be such as to yield a scattered electron wave function identical to Eq. (1). This simulation is perfectly acceptable so long as we only concern ourselves with the wave function in the bulk and not beyond the actual surface.

Thus we must position the hard wall a distance, d, to the right of the actual surface such that the wave function for this case

$$\phi_{\vec{k}}(\vec{r}) = 2ie^{ik_x d}\sin(k_x x - k_x d)\,e^{i\vec{k}_\parallel\cdot\vec{r}},\quad x \leqslant d \tag{2}$$

is the same as the actual wave function [Eq. (1) for $x \leqslant 0$]. That is

$$\begin{aligned} d &= \frac{\delta}{k_x} \\ &= \frac{1}{k_x}\arctan\left[\frac{k_x}{(2mV_0/\hbar^2 - k_x^2)^{1/2}}\right]\ . \end{aligned} \tag{3}$$

The problem of conduction-electron scattering by a contaminated surface is in this way modeled by scattering by a grid of randomly situated impurities a distance, d, in front of a hard wall. This is illustrated in Fig. 1.

B. Scattering by a single adsorbed impurity

We consider first the case of scattering from a single surface impurity with position $\vec{r}_i = (0, y_i, z_i) = (0, \vec{R}_i)$ and perturbing potential v_i. It is convenient to express the general theory in operator formalism. The Green's function operator, or resolvent, for the Hamiltonian that includes the hard wall is defined by[16]

$$\tilde{G}_0 \equiv \lim_{\epsilon \to 0} \frac{1}{E + i\epsilon - \tilde{H}_0} ,$$

where $E\ (= \hbar^2 k^2/2m)$ is the electron energy and $\tilde{H}_0$ is the hard-wall Hamiltonian

$$\tilde{H}_0(\vec{r}) = -\frac{\hbar^2 \nabla^2}{2m} + V_{\text{infinite step}} .$$

In configuration space, $\tilde{G}_0$ has the representation

$$\tilde{G}_0(\vec{r}, \vec{r}\,') = G_0(\vec{r}, \vec{r}\,') - G_0(\vec{r}, \bar{\vec{r}}\,')$$
$$= -\frac{2m}{4\pi \hbar^2} \left(\frac{e^{ik|\vec{r}-\vec{r}\,'|}}{|\vec{r}-\vec{r}\,'|} - \frac{e^{ik|\vec{r}-\bar{\vec{r}}\,'|}}{|\vec{r}-\bar{\vec{r}}\,'|} \right) , \quad (4)$$

where $G_0(\vec{r}, \vec{r}\,')$ is the well-known free-particle Green's function and $\bar{\vec{r}} \equiv (2d - x, y, z)$ is the image of $\vec{r} = (x,y,z)$.

$\tilde{G}_0(\vec{r}, \vec{r}\,')$ as given by Eq. (4) above is identical in form to the Green's function used by Greene and O'Donnell.[5] In the present work, however, the hard wall is no longer fixed at the surface but is displaced into the vacuum a distance, d, which varies with the angle of incidence of the electron on the surface, the electron energy, and the work function of the metal [Eq. (3)].

Next we will find it useful to use a t-matrix operator associated with the perturbing potential of the single adsorbed impurity and expressed in terms of the Hamiltonian that includes the hard wall. We label this operator $\tilde{t}_i$ and define it by

$$\tilde{t}_i \equiv v_i + v_i \tilde{G}_0 \tilde{t}_i . \quad (5)$$

The eigenstate, $\Psi_{\vec{k}}$, associated with the full Hamiltonian, $H \equiv \tilde{H}_0 + v_i$, is related to the eigenstate, $\Phi_{\vec{k}}$, of the unperturbed Hamiltonian, $\tilde{H}_0$, through the equation[17]

$$\Psi_{\vec{k}} = \Phi_{\vec{k}} + \tilde{G}_0 \tilde{t}_i \Phi_{\vec{k}} . \quad (6)$$

In configuration space, this equation has the form

$$\psi_{\vec{k}}(\vec{r}) = \phi_{\vec{k}}(\vec{r}) + \int \int \tilde{G}_0(\vec{r}, \vec{r}\,') \tilde{t}_i(\vec{r}\,', \vec{r}\,'')$$
$$\times \phi_{\vec{k}}(\vec{r}\,'')\, d^3r'\, d^3r'' . \quad (7)$$

It is important to recognize, however, that the physically accessible parameter is not the matrix element of $\tilde{t}_i$ that appears in Eq. (7) but rather the t matrix of the impurity *decoupled* from the surface. We label this quantity, t_i. It is the t matrix associated with the impurity positioned in the bulk, or, in a free-electron approximation, in free space. By analogy to Eq. (5), t_i may be defined by

$$t_i \equiv v_i + v_i G_0 t_i , \quad (8)$$

where G_0 is the free-electron Green's function. Note that by assuming the same potential for the impurity when it is located at the surface and in the bulk, we are ignoring differences in binding character between adsorbed and absorbed impurities. Although this assumption may be justifiable in certain instances (as for physically adsorbed atoms), it is not, in general, an accurate description of the actual case (as for chemisorbed atoms). Equation (7), therefore, represents an additional approximation, which we use to investigate the qualitative behavior of surface scattering, particularly as pertains to the effects of multiple scattering and interference phenomena.

The t matrix, t_i, has an immediate and simple physical significance in the momentum representation.[16] The matrix element of t_i between momentum states $\vec{k}\,'$ and $\vec{k}$ (corresponding to the same energy) is proportional to the scattering amplitude $f_{\vec{k} \to \vec{k}'}$ for elastic scattering from the incident state $\vec{k}$ to the scattered state $\vec{k}\,'$. Specifically, the relationship is

$$(\vec{k}\,'|t_i|\vec{k}) = -\frac{4\pi \hbar^2}{2m} f_{\vec{k} \to \vec{k}'} .$$

We would like, therefore, to express $\tilde{t}_i$, the t matrix for the adsorbed impurity, in terms of t_i, the t matrix for the impurity alone. This may be easily accomplished through some simple operator algebra.[15] The result is

$$\tilde{t}_i = t_i \frac{1}{1 - G_1 t_i} , \quad (9)$$

where

$$G_1 \equiv \tilde{G}_0 - G_0 .$$

We next wish to investigate the representation of $\tilde{t}_i$ in configuration space, in preparation for an analysis of the actual scattered wave function. In order to find $\tilde{t}_i(\vec{r}, \vec{r}\,')$, it is necessary to know $t_i(\vec{r}, \vec{r}\,')$.

We will assume that the perturbing potential, $v_i(\vec{r})$, when situated in the bulk, is highly localized and scatters conduction electrons isotropically. For such an impurity, the corresponding t-matrix real-space matrix element is given by

$$t_i(\vec{r}, \vec{r}\,') = \alpha f_k \delta(\vec{r} - \vec{R}_i) \delta(\vec{r}\,' - \vec{R}_i) , \quad (10)$$

where $f_{\vec{k}}$ is the s-wave scattering amplitude and $\alpha = -4\pi \hbar^2/2m$. This approximation ignores any angle dependence of the scattering center in the bulk. For metals the de Broglie wavelength of a conduction electron is of the order of an angstrom and a typical impurity has a range of the same order of magnitude. Some angle dependence is, therefore, actually expected, probably including p-wave and, perhaps even, d-wave scattering. The s-wave approximation is nevertheless a plausible first approximation for screened impurities in a bulk metal and is superior to a Born approximation. Furthermore, in the adsorbed state, the surface potential and the extent of disorder (contamination) will tend to dominate the detailed scattering behavior of the individual impurities and make still more reasonable their characterization as *s*-wave scatterers for the problem at hand.

In configuration space, Eq. (9) takes the form

$$\tilde{t}_i(\vec{r},\vec{r}\,') = \frac{\alpha f_k \delta(\vec{r}-\vec{R}_i)\delta(\vec{r}\,'-\vec{R}_i)}{1+\alpha f_k G_0(\vec{R}_i,\vec{\bar{R}}_i)}$$

$$\equiv \tilde{t}(k)\delta(\vec{r}-\vec{R}_i)\delta(\vec{r}\,'-\vec{R}_i) \ . \qquad (11)$$

Equation (11) expresses the scattering properties of the impurity in the adsorbed state. The δ functions characterize the impurity as a very short-range scattering center and the multiplying factor, $\tilde{t}(k)$, exhibits the multiple-scattering property when coupled to the surface potential. If we write $\tilde{t}(k)$ explicity as a geometric series and observe that

$$G_0(\vec{R}_i,\vec{\bar{R}}_i) = \frac{1}{\alpha} e^{2ikd}/2d \ ,$$

we have

$$\tilde{t}(k) = \alpha\left[f_k - f_k \frac{e^{2ikd}}{2d} f_k + f_k \frac{e^{2ikd}}{2d} f_k \frac{e^{2ikd}}{2d} f_k - \cdots \right] . \qquad (12)$$

Here $\tilde{t}(k)$ has a clear physical interpretation. A Bloch wave incident upon the adsorbed impurity is partially scattered off into the bulk with scattering amplitude f_k. Part of the Bloch wave, however, is scattered to interact with the surface potential (displaced hard wall) and there suffers a phase change of π (hence the negative sign). As the wave moves away from the wall, it interacts with the impurity again and repeats the above process *ad infinitum.* During each transit between impurity and wall and back again to impurity (through a distance $2d$) there is an additional phase change of $2kd$ and a reduction in amplitude proportional to $1/2d$. The hard wall acts as a "mirror" and appears to emit scattered wavefronts from the impurity's "image".

The total scattered wave is a superposition of all multiply-scattered waves that move off into the bulk. This superposition appears formally in the second term of the right-hand side of Eq. (7). Waves leaving from the wall without additional interaction with the impurity and those that strike the wall first are included through the multiplying factor $\tilde{G}_0(\vec{r},\vec{r}\,')$ (as distinguished from a free-electron Green's function).

C. Scattering by a random coverage of adsorbed impurity

Having observed the manner in which a single adsorbed impurity scatters a conduction electron, we may now discuss the scattering from a surface with many adsorbed impurities. In analogy to Eq. (6), we write the general scattering equation as

$$\Psi_{\vec{k}} = \Phi_{\vec{k}} + \tilde{G}_0 \tilde{T} \Phi_{\vec{k}} \ . \qquad (13)$$

Here $\Psi_{\vec{k}}$ is the conduction-electron eigenstate associated with the entire contaminated surface; $\Phi_{\vec{k}}$ is the eigenstate associated with the clean state; and $\tilde{T}$ is the *t*-matrix operator (with the hard-wall Hamiltonian) corresponding to the entire contaminated surface perturbation.

The surface perturbing potential, V, is given by the sum over the surface lattice of all individual impurity potentials, v_i. From Eq. (5), we may then write the total *t* matrix $\tilde{T}$, as

$$\tilde{T} = \sum_i v_i(1+\tilde{G}_0\tilde{T}) \ .$$

In order to express $\tilde{T}$, the *t* matrix associated with all the adsorbed impurities, in terms of $\tilde{t}_i$, the *t* matrix associated with an individual adsorbed impurity, we use a general procedure of multiple scattering theory (as described, for example, by Lax in a review paper on this subject[18]). We define

$$Q_i \equiv v_i(1+\tilde{G}_0\tilde{T}) = (1+\tilde{t}_i\tilde{G}_0)^{-1}\tilde{t}_i\left[1+\tilde{G}_0\sum_j Q_j\right] .$$

Simple algebra then gives

$$Q_i = \tilde{t}_i + \tilde{t}_i\tilde{G}_0 \sum_{j\neq i} Q_j \ , \qquad (14)$$

so that

$$\tilde{T} = \sum_i \tilde{t}_i + \sum_i \sum_{j\neq i} \tilde{t}_i\tilde{G}_0\tilde{t}_j + \sum_i \sum_{j\neq i} \sum_{l\neq j} \tilde{t}_i\tilde{G}_0\tilde{t}_j\tilde{G}_0\tilde{t}_l + \cdots \ . \qquad (15)$$

Equation (15) represents a standard multiple-scattering series. In the present context, it describes all possible combinations of multiple scatterings between individual adsorbed scattering centers and the surface potential.

The eigenstate corresponding to the contaminated surface is now given by

$$\Psi_{\vec{k}} = \Phi_{\vec{k}} + \tilde{G}_0\left[\sum_i \tilde{t}_i + \sum_i \sum_{j\neq i} \tilde{t}_i\tilde{G}_0\tilde{t}_j + \sum_i \sum_{j\neq i} \sum_{l\neq j} \tilde{t}_i\tilde{G}_0\tilde{t}_j\tilde{G}_0\tilde{t}_l + \cdots \right]\Phi_{\vec{k}} \ . \qquad (16)$$

If no multiple scattering between adsorbed impurities were considered, the following approximation would replace the above result:

$$\Psi_{\vec{k}} \approx \Phi_{\vec{k}} + \tilde{G}_0 \sum_i \tilde{t}_i \Phi_{\vec{k}} = \Phi_{\vec{k}} + \tilde{G}_0 \sum_i t_i \left(\frac{1}{1-G_1 t_i}\right)\Phi_{\vec{k}} \ .$$

If, finally, the single impurity scattering problem were performed in Born approximation [so that Eq.

(8) was truncated to $\tilde{t}_i \approx v_i$], the general scattering equation would appear as

$$\Psi_{\vec{k}} \approx \Phi_{\vec{k}} + \tilde{G}_0 \sum_i v_i \Phi_{\vec{k}} = \Phi_{\vec{k}} + \tilde{G}_0 V \Phi_{\vec{k}} \; . \tag{17}$$

Equation (17) is the starting point for the Greene and Malamus theory of conduction-electron surface scattering from adsorbed impurities.

As in the Greene and Malamus theory, we now note that an equation such as Eq. (16) refers to the scattered state arising from some specific configuration of impurities randomly adsorbed onto a surface. Even if we were theoretically capable of describing a model for such a configuration, the problem of counting surface lattice sites is evidently a statistical one. The pertinent quantity is, therefore, not the exact scattered wave but rather the average scattered wave.

We represent the surface statistically by an ensemble of contamination configurations and denote the averaging process by the symbol $\langle\;\rangle$. Equation (16) then gives the average scattered state as

$$\langle \Psi_{\vec{k}} \rangle = \Phi_{\vec{k}} + \tilde{G}_0 \left(\sum_i \langle \tilde{t}_i \rangle + \sum_i \sum_{j \neq i} \langle \tilde{t}_i \tilde{G}_0 \tilde{t}_j \rangle + \sum_i \sum_{j \neq i} \sum_{l \neq j} \langle \tilde{t}_i \tilde{G}_0 \tilde{t}_j \tilde{G}_0 \tilde{t}_l \rangle + \cdots \right) \Phi_{\vec{k}} \; . \tag{18}$$

This general equation is exact within the context of any model of clean-state surface potential and adsorbate overlayer. However, the actual calculation of averaged quantities like

$$\langle \tilde{t}_i \tilde{G}_0 \tilde{t}_j \rangle, \quad i \neq j$$

and

$$\langle \tilde{t}_i \tilde{G}_0 \tilde{t}_j \tilde{G}_0 \tilde{t}_l \rangle, \quad i \neq j \neq l$$

requires a theory for the correlation between adsorbed impurities located at different metal surface sites. This is, in general, a complicated and presently not well-understood problem.[19,20] We, therefore, assume a totally random array of surface impurities (as in the Greene and O'Donnell and Greene and Malamus theories). This allows us to assume statistical independence and write

$$\langle \tilde{t}_i \tilde{G}_0 \tilde{t}_j \rangle = \langle \tilde{t}_i \rangle \tilde{G}_0 \langle \tilde{t}_j \rangle, \quad i \neq j \; . \tag{19}$$

But note that, even for a totally uncorrelated array of adsorbed atoms, it is *not* completely correct to write for higher-order terms

$$\langle \tilde{t}_i \tilde{G}_0 \tilde{t}_j \tilde{G}_0 \tilde{t}_l \rangle = \langle \tilde{t}_i \rangle \tilde{G}_0 \langle \tilde{t}_j \rangle \tilde{G}_0 \langle \tilde{t}_l \rangle, \quad i \neq j \neq l \; . \tag{20}$$

This is because the same lattice contribution may occur more than once in such an expression. That is, in Eq. (20), the subscripts i and l may refer to the same lattice site. Nevertheless, we use Eq. (20) and its generalizations to higher-order terms as an approximation. It clearly represents a reasonable model in which to formulate an analysis of multiple scattering and interference effects of electron surface scattering. In fact, this approximation is well known in the theory of binary alloys as the average-t-matrix approximation (ATA).[21–23]

In view of the preceding discussion, the average scattered state of a surface-scattered conduction electron is now given by

$$\langle \Psi_{\vec{k}} \rangle = \Phi_{\vec{k}} + \tilde{G}_0 \left(\sum_i \langle \tilde{t}_i \rangle + \sum_i \sum_{j \neq i} \langle \tilde{t}_i \rangle \tilde{G}_0 \langle \tilde{t}_j \rangle + \sum_i \sum_{j \neq i} \sum_{l \neq j} \langle \tilde{t}_i \rangle \tilde{G}_0 \langle \tilde{t}_j \rangle \tilde{G}_0 \langle \tilde{t}_l \rangle + \cdots \right) \Phi_{\vec{k}} \; . \tag{21}$$

Equation (21), which explicitly exhibits the surface average-t-matrix approximation, can be given a convenient pictorial interpretation. The approximation is equivalent to replacing the contaminated surface with its actual *disordered* array of perturbing potentials, v_i, by an *ordered* array of ficticious, or "coherent", potentials, η_i, with η_i defined by

$$\langle \tilde{t}_i \rangle \equiv \eta_i (1 + \tilde{G}_0 \langle \tilde{t}_i \rangle) \; . \tag{22}$$

In this correspondence the perturbing potentials, v_i, randomly occupy the surface lattice but the coherent potentials occupy *every* surface lattice site. Equation (22) defines the coherent potential, η_i, as that potential whose t matrix (with the hard-wall Hamiltonian) is just the average t matrix of the actual impurity configuration (with the hard-wall Hamiltonian).

To see this correspondence, note that, by the same argument that led to Eq. (15), the t matrix corresponding to the sheet of coherent potential will be given by the multiple-scattering series

$$\begin{aligned} \tilde{T}_{\text{cp}} &\equiv \sum_i \eta_i (1 + \tilde{G}_0 \tilde{T}_{\text{cp}}) \\ &= \sum_i \langle \tilde{t}_i \rangle + \sum_i \sum_{j \neq i} \langle \tilde{t}_i \rangle \tilde{G}_0 \langle \tilde{t}_j \rangle \\ &\quad + \sum_i \sum_{j \neq i} \sum_{l \neq j} \langle \tilde{t}_i \rangle \tilde{G}_0 \langle \tilde{t}_j \rangle \tilde{G}_0 \langle \tilde{t}_l \rangle + \cdots \; . \end{aligned}$$

But by application of Eq. (13), the scattered state arising from the lattice of coherent potential is identical to the average scattered state of the actual contaminated surface.

Thus, the problem of conduction-electron scattering by a contaminated surface is formally reduced to a consideration of scattering by a grid of coherent potential positioned a distance, d (which is a function of the electron angle of incidence on the surface) in front of a hard wall. This calculation is discussed in Sec. III.

III. SCATTERING AMPLITUDES OF THE AVERAGE SCATTERED WAVE

A. Scattering from a grid of coherent potential in front of a hard wall

Here we investigate the way that the conduction electron is scattered in the model discussed above. The situation is schematized in Fig. 2.

The average scattered state is given by Eq. (21). Alternatively, using Eqs. (13) and (14), we may write

$$\langle \Psi_{\vec{k}} \rangle = \Phi_{\vec{k}} + \tilde{G}_0 \sum_i \langle \tilde{t}_i \rangle \left[1 + \tilde{G}_0 \sum_{j \neq i} \langle Q_j \rangle \right] \Phi_{\vec{k}} \ , \tag{23}$$

where

$$\langle Q_j \rangle \equiv \langle \tilde{t}_j \rangle + \langle \tilde{t}_j \rangle \tilde{G}_0 \sum_{l \neq j} \langle Q_l \rangle \ . \tag{24}$$

As discussed by Lax in his review of multiple scattering theory[18] and later utilized by McRae[24] in a theoretical analysis of low-energy electron diffraction from perfect crystals, it is instructive in multiple-scattering phenomena to define an "effective" state. This state may be viewed as the net incident state (after repeated multiple scattering) that is scattered by an individual scattering center. In the present context, we define this state as

$$\Psi^i_{\vec{k}} \equiv \left[1 + \tilde{G}_0 \sum_{j \neq i} \langle Q_j \rangle \right] \Phi_{\vec{k}} \ , \tag{25}$$

so that the average scattered state can be written

$$\langle \Psi_{\vec{k}} \rangle = \Phi_{\vec{k}} + \tilde{G}_0 \sum_i \langle \tilde{t}_i \rangle \Psi^i_{\vec{k}} \ . \tag{26}$$

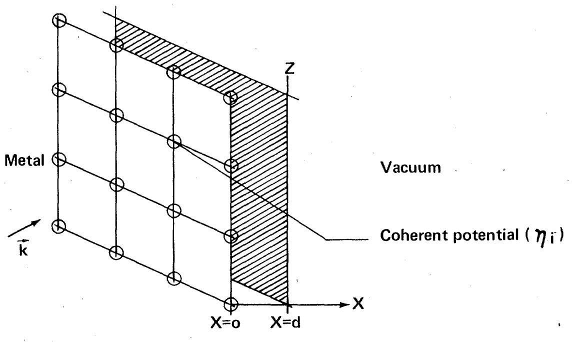

FIG. 2. Scattering by a grid of coherent potential before a hard wall.

From Eqs. (24) and (25) we obtain

$$\langle Q_j \rangle \Phi_{\vec{k}} = \langle \tilde{t}_j \rangle \left[1 + \tilde{G}_0 \sum_{l \neq j} \langle Q_l \rangle \right] \Phi_{\vec{k}} = \langle \tilde{t}_j \rangle \Psi^j_{\vec{k}} \ .$$

Thus

$$\Psi^i_{\vec{k}} = \Phi_{\vec{k}} + \tilde{G}_0 \sum_{j \neq i} \langle \tilde{t}_j \rangle \Psi^j_{\vec{k}} \ . \tag{27}$$

If the surface impurity is randomly adsorbed onto surface lattice sites with a concentration, c, then the ensemble of uncorrelated surface contamination configurations will yield probabilities of impurity adsorption and no adsorption at the ith lattice site equal to c and $(1-c)$, respectively. Thus, the average t matrix at the ith site is given simply by $\langle \tilde{t}_i \rangle = c\tilde{t}_i$. In view of this and Eq. (11), Eqs. (26) and (27) become in coordinate space and for the case of s-wave scattering impurities

$$\langle \psi_{\vec{k}}(\vec{r}) \rangle = \phi_{\vec{k}}(\vec{r}) + \sum_i \tilde{G}_0(\vec{r}, \vec{R}_i) c\tilde{t}(k) \psi^i_{\vec{k}}(\vec{R}_i) \ , \tag{28}$$

$$\psi^i_{\vec{k}}(\vec{R}_i) = \phi_{\vec{k}}(\vec{R}_i) + \sum_{j \neq i} \tilde{G}_0(\vec{R}_i, \vec{R}_j) c\tilde{t}(k) \psi^j_{\vec{k}}(\vec{R}_j) \ . \tag{29}$$

Equation (28) has the following interpretation. The incident and scattered waves contained in this equation are to be thought of as propagating under the influence of the unperturbed surface potential (the tildes over the Green's function and t-matrix parameter denote this). $\phi_{\vec{k}}(\vec{r})$ and $\psi^i_{\vec{k}}(\vec{R}_i)$ are, therefore, described as "distorted" waves. $\psi^i_{\vec{k}}(\vec{R}_i)$ is the "effective" distorted wave that is incident on the coherent potential scattering center located at the ith surface lattice site. It is scattered there with scattering amplitude proportional to the parameter $c\tilde{t}(k)$ which includes all multiple scattering between the coherent potential and the unperturbed surface potential as outlined in the discussion following Eq. (12). The total averaged wave scattered by the entire disordered surface is then just the superposition of all waves emanating from each coherent potential on the grid plus the wave scattered by the unperturbed surface potential alone [i.e., the backscattered part of $\phi_{\vec{k}}(\vec{r})$]. Equation (29) exhibits $\psi^i_{\vec{k}}(\vec{R}_i)$ as a self-consistent superposition of the incident standing wave $\phi_{\vec{k}}(\vec{R}_i)$ and the scattered effective distorted waves coming from all the scattering centers except the ith site.

In order to solve for the average scattered wave $\langle \psi_{\vec{k}}(\vec{r}) \rangle$, it is necessary to first solve for the effective distorted wave $\psi^i_{\vec{k}}(\vec{R}_i)$ incident at the ith surface lattice site. This may be easily accomplished because the *averaged* contaminated surface exhibits two-dimensional periodicity (as illustrated in Fig. 2) so that the *averaged* scattered wave must obey a two-dimensional Bloch condition. This requires that the effective distorted wave also satisfy this Bloch condition. Thus we may write

$$\psi^{L}_{\vec{k}}(\vec{R}_j) = e^{i\vec{k}_{\parallel}\cdot(\vec{R}_j - \vec{R}_i)}\psi^{L}_{\vec{k}}(\vec{R}_i) \; . \tag{30}$$

Substitution of Eq. (30) into Eq. (29) with a change of the dummy summation index, then, yields

$$\psi^{L}_{\vec{k}}(\vec{R}_i) = \phi_{\vec{k}}(\vec{R}_i) + \left[\sum_{j\neq 0} \tilde{G}_0(\vec{0},\vec{R}_j) c\tilde{t}(k) e^{i\vec{k}_{\parallel}\cdot\vec{R}_j} \right] \psi^{L}_{\vec{k}}(\vec{R}_i) \tag{31}$$

or

$$\psi^{L}_{\vec{k}}(\vec{R}_i) = \frac{\phi_{\vec{k}}(\vec{R}_i)}{1 - \sum_{j\neq 0} \tilde{G}_0(\vec{0},\vec{R}_j) c\tilde{t}(k) e^{i\vec{k}_{\parallel}\cdot\vec{R}_j}} \; . \tag{32}$$

Equation (31) is a statement that the effective distorted Bloch wave incident on the ith scatterer is just the self-consistent superposition of the original unperturbed incident wave and the scattered waves emanating from all the other scatterers excited by the effective distorted Bloch wave. This interpretation of a Bloch wave is familiar from the case of three-dimensional bulk crystals (cf. Kohn and Rostoker,[25] Korringa,[26] and Ziman[27]). In that case, however, there is no homogeneous part of the wave function analogous to $\phi_{\vec{k}}(\vec{r})$ since there is no unperturbed incident wave associated with a conduction electron in a bulk crystal. Also, the "distorted" Green's function in our equations is usually replaced by the free-electron Green's function in the bulk case.

We may now substitute Eq. (32) into Eq. (28) and, using Eqs. (2) and (4) for $\phi_{\vec{k}}$ and $\tilde{G}_0(\vec{r},\vec{r}\,')$, respectively, obtain

$$\langle\psi_{\vec{k}}(\vec{r})\rangle = \phi_{\vec{k}}(\vec{r}) - \frac{\dfrac{2ic\tilde{t}(k)}{\alpha} e^{ik_x d}(\sin k_x d) \left(\sum_i \dfrac{e^{ik|\vec{r}-\vec{R}_i|}}{|\vec{r}-\vec{R}_i|} - \sum_i \dfrac{e^{ik|\vec{r}-\vec{R}_i-2d\vec{e}_1|}}{|\vec{r}-\vec{R}_i-2d\,\vec{e}_1|} \right) e^{i\vec{k}_{\parallel}\cdot\vec{R}_i}}{1 - \dfrac{c\tilde{t}(k)}{\alpha} \sum_{j\neq 0} \left(\dfrac{e^{ik|\vec{R}_j|}}{|\vec{R}_j|} - \dfrac{e^{ik|\vec{R}_j+2d\vec{e}_1|}}{|\vec{R}_j+2d\,\vec{e}_1|} \right) e^{i\vec{k}_{\parallel}\cdot\vec{R}_j}} \; . \tag{33}$$

Here $\vec{e}_1$ is a unit vector in the x direction (perpendicular to the surface and pointing into the vacuum).

Equation (33) is the expression we have been seeking. It gives the averaged surface-scattered-conduction-electron wave function in terms of the primary parameters of interest. These include the concentration of adsorbate c; the angle of incidence of the conduction electron upon the surface (contained in k_x); the scattering strength of the adsorbate atom in the bulk [contained in $\tilde{t}(k)$] through Eq. (11); and the surface lattice parameter (contained in the lattice vector $\vec{R}_i$).

The numerator of the second term in Eq. (33) comprises the superposition of all waves arising from multiple-scattering combinations between a single coherent potential-scattering center and the unperturbed surface potential (displaced hard wall). The denominator of that term represents the modification, from the standing wave $\phi_{\vec{k}}(\vec{R}_i)$, in the effective distorted wave incident on a single coherent potential-scattering center. This modification stems from multiple scatterings between all the other coherent potentials on the surface and the unperturbed surface potential. A single scattering, or kinematic calculation would exclude the sum in the denominator. However, such a calculation still retains the effects of repeated scatterings between a single coherent potential-scattering center and the unperturbed surface potential.

B. Structure factor, $S(\vec{R},X)$, and averaged surface-scattering amplitudes

From Eq. (33), we see that we need to evaluate sums of the general form

$$S(\vec{R},X) \equiv \sum_j \frac{e^{ik|\vec{R}+\vec{X}-\vec{R}_j|}}{|\vec{R}+\vec{X}-\vec{R}_j|} e^{i\vec{k}_{\parallel}\cdot\vec{R}_j} \; , \tag{34}$$

where $\vec{r} = (\vec{R},X)$. McRae,[24] using a method developed by Ewald,[28] has shown that such a two-dimensional direct lattice sum may alternatively be expressed as a sum in the corresponding two-dimensional reciprocal lattice

$$S(\vec{R},X) = \frac{2\pi i}{A} \sum_g \frac{e^{i(k^2-|\vec{k}_{\parallel}+\vec{g}|^2)^{1/2}|x|}}{(k^2-|\vec{k}_{\parallel}+\vec{g}|^2)^{1/2}} e^{i(\vec{k}_{\parallel}+\vec{g})\cdot\vec{R}} \; . \tag{35}$$

Here A is the area of a unit surface cell and g is a two-dimensional reciprocal-lattice vector [for a square lattice $\vec{g} \equiv (2\pi/a)(n\,\vec{e}_2 + m\,\vec{e}_3)$ where n and m are integers and a is the lattice parameter].

We may now use Eq. (35) and the following definitions

$$K_{\vec{g}} \equiv (k^2 - |\vec{k}_{\parallel}+\vec{g}\,|^2)^{1/2} \; , \tag{36}$$

$$S' \equiv \sum_{j\neq 0} \left(\frac{e^{ik|\vec{R}_j|}}{|\vec{R}_j|} - \frac{e^{ik|\vec{R}_j+2d\vec{e}_1|}}{|\vec{R}_j+2d\,\vec{e}_1|} \right) e^{i\vec{k}_{\parallel}\cdot\vec{R}_j} \; , \tag{37}$$

to rewrite the averaged-surface-scattered wave as

$$\langle\psi_{\vec{k}}(\vec{r})\rangle=\phi_{\vec{k}}(\vec{r})+\frac{\frac{4\pi}{A}\frac{c\tilde{t}(k)}{\alpha}e^{ik_xd}\sin(k_xd)}{1-c\frac{\tilde{t}(k)}{\alpha}S'}\sum_{g}\left[\frac{e^{-iK_{\vec{g}}X}-e^{-K_{\vec{g}}X}e^{2iK_{\vec{g}}d}}{K_{\vec{g}}}\right]e^{i(\vec{k}_{\parallel}+\vec{g})\cdot\vec{R}}\ . \tag{38}$$

In Eq. (38), $\vec{r}$ is in the crystal bulk ($x<0$).

We want the scattering amplitudes, or reflection coefficients, of the averaged scattered wave. Thus we look at the asymptotic behavior of $\langle\psi_{\vec{k}}(\vec{r})\rangle$. In this region, away from the surface, the only waves that will survive are those for which $K_{\vec{g}}$ is real. There are also waves close to the surface for which $K_{\vec{g}}$ is pure imaginary. These waves are *evanescent* waves that travel along the surface but that decay exponentially away from it. They are the waves that were not included in the Greene and Malamus theory. It is apparent that the evanescent waves are important in forming the effective waves incident at the coherent potentials that give rise to the full averaged propagating wave and are necessary in a self-consistent scattering theory. However, far from the surface they vanish and, therefore, do not *directly* contribute to the far field.

Letting $\vec{K}_0^-\equiv(-K_0,\vec{k}_{\parallel}+\vec{g})$ be the wave vector corresponding to a diffracted wave and substituting for $\phi_{\vec{k}}(\vec{r})$, we have far from the surface

$$\psi_{\vec{k}}(\vec{r})=e^{i\vec{k}\cdot\vec{r}}-e^{2ik_xd}e^{i\bar{\vec{k}}\cdot\vec{r}}+\frac{\frac{4\pi}{A}\frac{c\tilde{t}(k)}{\alpha}e^{ik_xd}(\sin k_xd)}{1-c\frac{\tilde{t}(k)}{\alpha}S'}\sum_{\substack{\vec{g}\\ K_{\vec{g}}\text{real}}}\left[\frac{1-e^{2iK_{\vec{g}}d}}{K_{\vec{g}}}\right]e^{i\vec{K}_{\vec{g}}^-\cdot\vec{r}}\ .$$

Noting that $K_0=k_x$ and $\vec{K}_0^-=\bar{\vec{k}}\equiv(-k_x,k_{\parallel})$ (i.e., the zeroth-order diffracted wave is just the specularly reflected wave), we may rewrite the averaged scattered wave away from the surface as

$$\langle\psi_{\vec{k}}(\vec{r})\rangle=e^{i\vec{k}\cdot\vec{r}}+R_{\bar{\vec{k}}}e^{i\bar{\vec{k}}\cdot\vec{r}}+\sum_{\substack{g\neq0\\ K_{\vec{g}}\text{real}}}R_{\vec{K}_{\vec{g}}^-}e^{i\vec{K}_{\vec{g}}^-\cdot\vec{r}}\ , \tag{39}$$

where

$$R_{\bar{\vec{k}}}=-e^{2ik_xd}\left[1+\frac{[8\pi ic\tilde{t}(k)/A\alpha]\sin^2k_xd}{(1-[c\tilde{t}(k)/\alpha]S')k_x}\right]\ , \tag{40}$$

$$R_{\vec{K}_{\vec{g}}^-}=\frac{[4\pi c\tilde{t}(k)/A\alpha]e^{ik_xd}\sin k_xd}{(1-[c\tilde{t}(k)/\alpha]S')}\left[\frac{1-e^{2iK_{\vec{g}}d}}{K_{\vec{g}}}\right]\ . \tag{41}$$

C. Probabilities for specular reflection and higher-order diffracted waves

Equations (40) and (41) represent the reflection coefficients, or scattering amplitudes, of the specular and higher-order diffracted waves contained in the averaged-surface-scattered wave. We now briefly discuss how these quantities are related to the corresponding probabilities for specular reflection and higher-order diffraction. The correspondence is especially simple for the case of a spherical Fermi-surface model.

Let $\delta\psi_{\vec{k}}\equiv\psi_{\vec{k}}-\langle\psi_{\vec{k}}\rangle$ be the fluctuating difference between the conduction-electron wave function associated with one particular surface contamination configuration and the averaged wave function obtained from the entire ensemble of contamination configurations. Since the averaged fluctuation vanishes, the averaged probability current density is

$$\langle\vec{J}_{\vec{k}}\rangle=\frac{\hbar}{m}\text{Im}(\langle\psi_{\vec{k}}\rangle^*\nabla\langle\psi_{\vec{k}}\rangle)+\frac{\hbar}{m}\text{Im}\langle\delta\psi_{\vec{k}}^*\nabla\delta\psi_{\vec{k}}\rangle\ . \tag{42}$$

The first term of Eq. (42) represents the current density associated with the averaged surface-scattered wave. It is equivalently the current density associated with a conduction electron scattered by the coherent-potential-grid–displaced-hard-wall scattering mechanism. The remaining second part of the averaged current density is associated with the fluctuations from the averaged scattered wave. These fluctuations comprise the diffuse background of chiefly randomly scattered waves that also emergy from the contaminated surface.

In the present work, we are concerned with the nondiffuse scattered waves that emerge from the contaminated surface. Thus, we fix our interest on the current density of the averaged scattered wave. The current densities corresponding to the specular and higher-order diffracted waves contained in $\langle\psi_{\vec{k}}\rangle$ are given [using Eq. (39)] respectively by

$$\vec{J}_{\bar{\vec{k}}}=\frac{\hbar}{m}\bar{\vec{k}}\,|R_{\bar{\vec{k}}}'|^2$$

and

$$\vec{J}_{\vec{K}_{\vec{g}}^-}=\frac{\hbar}{m}\vec{K}_{\vec{g}}^-|R_{\vec{K}_{\vec{g}}^-}|^2\ ,$$

while the current density corresponding to the incident conduction-electron wave is just $\vec{J}_{\text{inc}} = (\hbar/m)\,\vec{k}$.

The *probability fluxes* associated with the specularly reflected, diffracted, and incident waves are the projections of corresponding current densities onto unit surface area and are given respectively by

$$I_{\vec{\bar{k}}} = \frac{\hbar}{m} k_x |R_{\vec{\bar{k}}}|^2 \ , \quad I_{\vec{K}^{-}_{\vec{g}}} = \frac{\hbar}{m} K_{\vec{g}} |R_{\vec{K}^{-}_{\vec{g}}}|^2 \ ,$$

$$I_{\text{inc}} = \frac{\hbar}{m} k_x \ .$$

The actual probabilities for specularly reflected and higher-order diffracted waves are then simply the ratios of associated probability fluxes to the incident probability flux. That is

$$P_s = |R_{\vec{\bar{k}}}|^2$$

and

$$P_{\vec{K}^{-}_{\vec{g}}} = \frac{K_{\vec{g}}}{k_x} |R_{\vec{K}^{-}_{\vec{g}}}|^2 \ , \tag{43}$$

where $R_{\vec{\bar{k}}}$ and $R_{\vec{K}^{-}_{\vec{g}}}$ are given by Eqs. (40) and (41).

D. Structure factor S'

In order to finally evaluate the probability functions appearing in Eq. (43), it is first necessary to evaluate the structure factor, S', that appears in Eqs. (40) and (41). S', recall, is defined by Eq. (37) as

$$S' = S_1' + S_2' \ ,$$

where we now define

$$S_1' \equiv \sum_{j \neq 0} \frac{e^{ik|\vec{R}_{\vec{j}}|}}{|\vec{R}_{\vec{j}}|} e^{i\vec{k}_{\parallel}\cdot\vec{R}_{\vec{j}}}$$

and

$$S_2' \equiv \sum_{j \neq 0} \frac{e^{ik|\vec{R}_{\vec{j}} + 2d\,\vec{e}_1|}}{|\vec{R}_{\vec{j}} + 2d\,\vec{e}_1|} e^{i\vec{k}_{\parallel}\cdot\vec{R}_{\vec{j}}} \ .$$

We wish to evaluate the sum, S', for a square lattice. Both S_1' and S_2' converge too slowly to be evaluated directly. We may use McRae's[24] application of the Ewald technique to accelerate the convergence of S_1'. This method is not applicable to S_2'. However, a simpler method can be used for S_2^1 (which, conversely, is not applicable to S_1'). We use Eq. (35) to transform S_2' completely into a sum in the reciprocal lattice minus the contributing term at the origin. This is just

$$S_2' = \frac{2\pi i}{A} \sum_{g} \frac{e^{2i(k^2 - |\vec{k}_{\parallel} + \vec{g}|^2)^{1/2} d}}{(k^2 - |\vec{k}_{\parallel} + \vec{g}|^2)^{1/2}} - \frac{e^{2ikd}}{2d} \ .$$

The square-root factor in this equation quickly becomes pure imaginary yielding a rapidly decreasing exponential term and consequently a rapidly converging expression for S_2'.

We have evaluated the sum, S', using the above methods for a square lattice of lattice parameter a. The details of the calculation are tedious but straightforward. The result is

$$S' = \frac{e^{2ikd}}{2d} - ik\left[1 + \operatorname{erf}\left(\frac{ik}{2E}\right)\right] - \frac{2E}{\sqrt{\pi}} e^{k^2/4E^2} + \frac{2\pi i}{A k_x}\left[1 + \operatorname{erf}\left(\frac{ik_x}{2E}\right) - e^{2ik_x d}\right] + SD + \frac{2\pi i}{A} SR \ . \tag{44}$$

Here E is an optimization parameter in the Ewald technique, erf is the error function with a complex argument and

$$SD = 2\sum_{n=1}^{\infty} [\cos(ak_y n) + \cos(ak_z n)] \left(\frac{\cos(akn) - \operatorname{Re} e^{iakn} \operatorname{erf}(aEn + ik/2E)}{an} \right)$$
$$+ 2\sum_{n=1}^{\infty}\sum_{m=1}^{\infty} \cos(ak_y n + ak_z m) \left(\frac{\cos ak(n^2+m^2)^{1/2} - \operatorname{Re}[e^{iak(n^2+m^2)^{1/2}} \operatorname{erf}(aE(n^2+m^2)^{1/2} + ik/2E)]}{a(n^2+m^2)^{1/2}} \right) \ ,$$

$$SR = \sum_{n=1}^{\infty} [G(K(n,0)) + G(K(-n,0)) + G(K(0,n)) + G(K(0,-n))]$$
$$+ \sum_{n=1}^{\infty}\sum_{m=1}^{\infty} [G(K(n,m)) + G(K(n,-m)) + G(K(-n,m)) + G(K(-n,-m))] \ ,$$

where

$$G(K(n,m)) \equiv \frac{1}{K(n,m)} \left[1 + \operatorname{erf}\left(\frac{iK(n,m)}{2E}\right) - e^{2idK(n,m)}\right]$$

and

$$K(n,m) \equiv \left[k_x^2 - \left(\frac{2\pi}{a}\right)^2 (n^2+m^2) - \frac{4\pi}{a}(k_y n + k_z m)\right]^{1/2} \ .$$

IV. MODEL CALCULATIONS

For our model calculations we have considered metals such as gold and copper for which a free-electron approximation is plausible. To avoid unnecessary complication, we treat only the case of their nonreconstructured (100) surfaces. Values used for these metals of the parameters pertinent to the present theory, the Fermi wave vector, k, the step parameter, V_0 (which is the sum of the work function and Fermi energy), and the surface lattice parameter, a, were extracted from Refs. 29–31.

Table I gives information concerning the presence of surface diffracted conduction-electron waves for various values of the electron angle of incidence (relative to the surface plane) on gold and copper contaminated (100) surfaces. We will see later that the presence of diffracted waves has an important effect on the conduction-electron probability of specular reflection.

According to Eq. (39), a propagating diffracted wave with wave vector $\vec{K}^{-}_{\vec{g}} \equiv (-K_{\vec{g}}, \vec{k}_{\parallel}+\vec{g})$ arises when $K^2_{\vec{g}} \equiv k^2 - |\vec{k}_{\parallel}+\vec{g}|^2$ is greater than zero. For the surfaces considered, only one diffracted wave is possible. The angle ϕ is the azimuthal angle measured in the surface plane [i.e., $\phi = \arctan(k_z/k_y)$]. For both metals, when ϕ is less than 45°, the diffracted wave is associated with the reciprocal-lattice vector $\vec{g}_1 \equiv (2\pi/a)\,\vec{e}_2$ (ϕ greater than 45° yields equivalent results due to the symmetry of the square surface lattice). The condition for a diffracted wave is then

TABLE I. The diffraction angle, θ_D, as a function of the electron angle of incidence, θ, and azimuthal angle, ϕ, for gold and copper (100) surfaces.

Metal		Au	Cu
ϕ °	θ °		θ_D °
0	0	35.0	35.9
0	6	34.4	35.4
0	12	32.7	33.7
0	18	29.7	30.8
0	24	25.1	26.3
0	30	17.6	19.3
0	36	···	···
0	42	···	···
0	48	···	···
0	54	···	···
0	60	···	···
15	0	26.9	28.8
15	6	26.3	27.5
15	12	24.4	25.7
15	18	21.0	22.4
15	24	14.9	16.8
15	30	···	2.8
15	36	···	···
15	42	···	···
15	48	···	···
15	54	···	···
15	60	···	···

$$k^2 \sin\theta + \frac{4\pi}{a} k \cos\phi \cos\theta - \frac{4\pi^2}{a^2} > 0 \tag{45}$$

and the maximum angle θ for which diffraction occurs for given values of k, a, and θ is the solution of the quadratic equation

$$-\cos^2\theta + \left[\frac{4\pi}{ka}\cos\phi\right]\cos\theta + \left[1 - \frac{4\pi^2}{k^2a^2}\right] = 0 \ . \tag{46}$$

For gold and copper (100) contaminated surfaces and $\phi = 0$°, no diffracted wave arises for θ greater than 34.98° and 35.92°, respectively. For $\phi = 15$°, these cutoff angles are, respectively, 28.93° and 30.15°.

Table I gives the angle, θ_D, that the diffracted wave vector makes with its surface plane projection [i.e., $\theta_D = \arcsin(K_g/k)$] as a function of the electron angle of incidence, θ and ϕ. As θ approaches a cutoff angle, for a particular value of ϕ, the diffraction angle, θ_D, monotonically approaches zero.

Our primary purpose has been to calculate a conduction-electron probability of specular reflection, P_s, as a function of its angle of incidence θ on a contaminated metal surface of varying impurity concentration and impurity scattering strength. Accordingly, Figs. 3–7 all represent plots of P_s vs θ for contaminated surfaces of the metals considered. Curves labeled MS (Figs. 5 and 6) or unspecified are obtained from the full multiple-scattering formula of the present theory as represented by Eqs. (43) and (40). Curves labeled SS (Figs. 5 and 6) correspond to a single-scattering calculation as described at the end of Sec. III A (i.e., $S'=0$).

Figure 4 also contains a plot of the electron probability of nondiffuse scattering, $P_{\rm nd}$, versus its angle of incidence, θ. In the case of no diffraction, this is the same as the probability of specular reflection. However, when a diffracted wave is also present, $P_{\rm nd}$ differs from P_s by the extra probability of the occurrence of the diffracted wave. That is, in general

$$\begin{aligned} P_{\rm nd} &= P_s + P_{\vec{K}^{-}_{\vec{g}}} \\ &= |R_{\vec{k}}^{-}|^2 + \frac{K_{\vec{g}}}{k_x}|R_{\vec{K}^{-}_{\vec{g}}}|^2 \end{aligned} \tag{47}$$

as given in Eqs. (43), (40), and (41). Here $K_{\vec{g}}$ is necessarily real.

The behavior of the electron probability of specu-

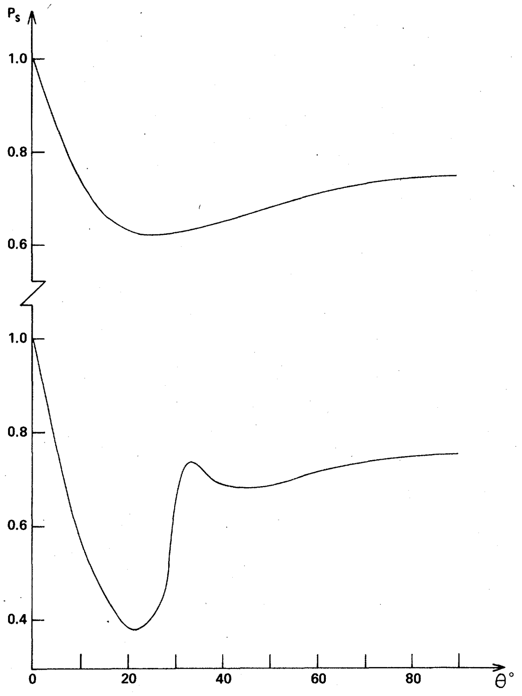

FIG. 3. Resonance. Copper (100) surface, $\delta=\frac{1}{2}\pi$, $C=0.9$. Upper curve: $\phi=45°$, lower curve: $\phi=15°$.

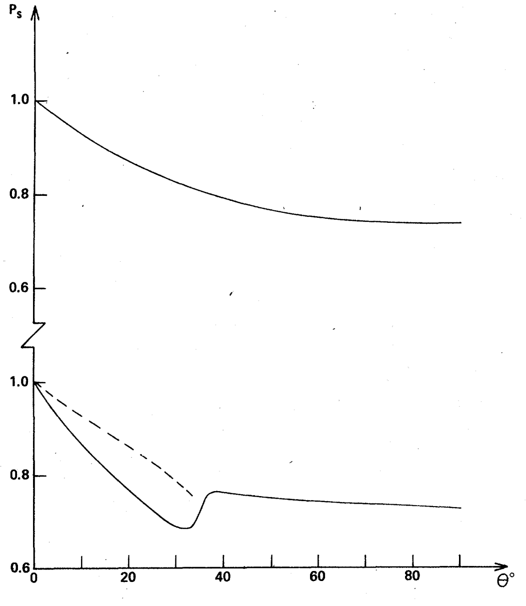

FIG. 4. Resonance. Gold (100) surface, $\delta=\frac{1}{3}\pi$, $C=0.5$. Upper curve: $\phi=45°$, lower curves: $\phi=0°$ ——P_s, - - -P_{nd}.

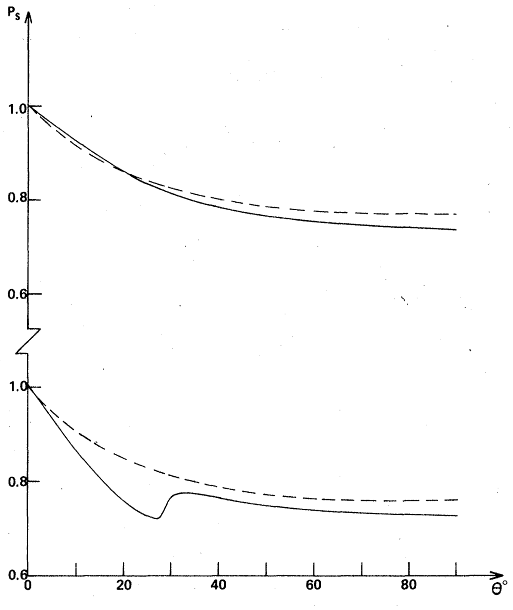

FIG. 5. Multiple scattering vs single scattering. Gold (100) surface, $\delta=\frac{1}{3}\pi$, $C=0.5$. Upper curves: $\phi=30°$, lower curves: $\phi=15°$ ——MS, - - -SS.

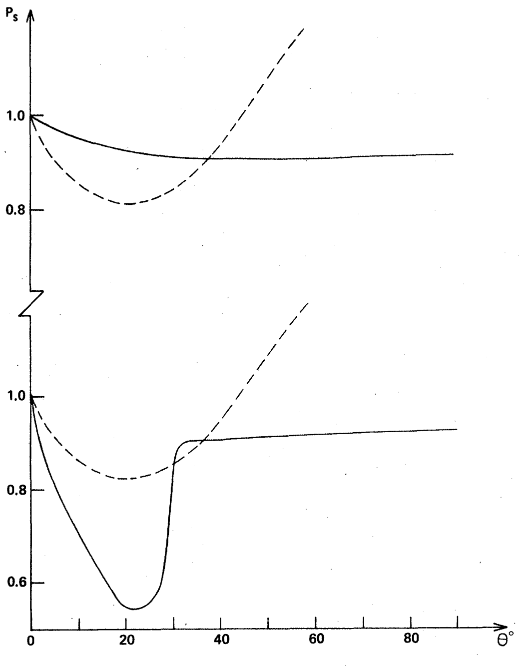

FIG. 6. Multiple scattering vs single scattering. Gold (100) surface, $\delta=\frac{1}{3}\pi$, $C=0.9$. Upper curves: $\phi=30°$, lower curves: $\phi=15°$ ——MS, - - -SS.

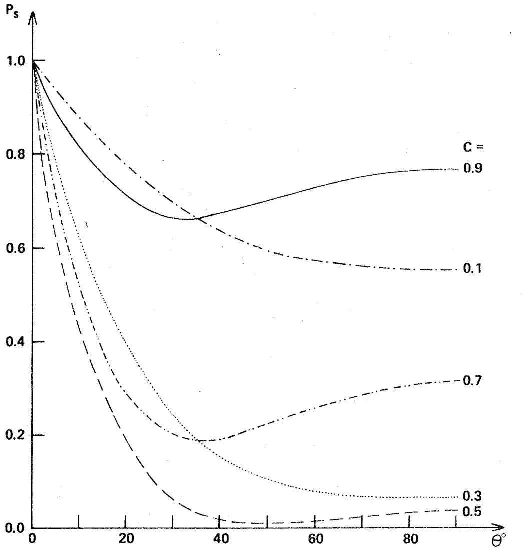

FIG. 7. Nordheim dependence. Copper (100) surface, $\delta = \frac{1}{2}\pi$, $\phi = 30°$.

lar reflection is compared in the various figures for different values of impurity concentration, C, and also the impurity scattering strength. This latter quantity is here measured by the impurity s-wave partial wave phase shift, δ. The relevant parameter which explicitly occurs in the equations for P_s and $P_{\rm nd}$ is the scattering amplitude, f_k, of the impurity when located in the bulk [Eq. (12)]. In our model of isotropic impurities, f_k is simply the first term of a partial wave expansion. That is

$$f_k = \frac{1}{k} e^{i\delta} \sin\delta \ .$$

V. DISCUSSION OF RESULTS

A. Resonances

The most striking feature of the present theory is the prediction of a *resonance* in the conduction-electron specular probability as a function of its angle of incidence on the contaminated surface. The resonance *arises from multiple scattering* of the conduction-electron wave between adsorbed impurities and is associated with the ability of the surface to diffract the incident electron as well as to specularly reflect it.

In Figs. 3–6, the lower curve illustrates the resonance effect. The upper curve corresponds to the identically contaminated surface but to the case of no diffraction (due to a different value of the electron azimuthal angle, ϕ). The upper curve, therefore, depicts the corresponding nonresonance situation.

The resonance property is exhibited as a qualitative deviation, from the corresponding nonresonance case, that takes the form of a *dent* or a *bump* (or both) in the specular probability curve. More specifically, the specular probability, for the resonance situation, behaves as follows. It decreases from unity at glancing incidence and either falls below (dent) or rises above (bump) the corresponding nonresonance curve until, in the vicinity of a *resonance angle,* it rapidly recovers. Thereafter, it closely approximates the nonresonance curve.

Figure 3 illustrates a dent and bump resonance corresponding to a copper (100) surface with azimuthal angle equal to 15°. The bump arises as the resonance curve overshoots the nonresonance curve before returning to the nonresonant behavior. The resonance occurs, in this case, near $\theta = 30.15°$. Figure 4 illustrates a dent resonance corresponding to a gold (100) surface with azimuthal angle equal to 0°. Here the resonance is near $\theta = 34.98°$. The case of a resonance for a gold (100) surface with azimuthal angle equal to 15° is given in Figs. 5 and 6, where the resonance occurs near $\theta = 28.93°$. Note that these resonance angles are just the *cutoff* angles (cited and discussed in Sec. IV) at which the corresponding surfaces cease to diffract the incident electron wave.

Note, also, that the resonant behavior of the specular probability is contained in the curves representing the full multiple-scattering calculation but *not* in the curves representing the single-scattering calculation (see Figs. 5 and 6). As discussed in Sec. III, the single-scattering theory includes multiple scattering between a single impurity and the unperturbed surface potential but not multiple scattering between different adsorbed impurities. The resonance property, therefore, is associated with multiple scattering between adsorbate atoms.

To understand the resonant behavior in the specular probability, $P_s = |R_{\bar{\vec{k}}}|^2$, when a diffracted wave is present, recall from Eq. (40) that the factor $1/\{1 - c[\tilde{t}(k)/\alpha]S'\}$ gives the modification in $R_{\bar{\vec{k}}}$ that arises when multiple scattering between adsorbed impurities is considered. It is this factor that is responsible for the resonance effect. Putting $S' = 0$ yields the corresponding single-scattering result.

The sum S' is defined in Eq. (37) and may be interpreted physically as a superposition at the origin of all waves emitted from the surface lattice sites of coherent potential and their images as a consequence of incidence of the plane wave $e^{i\vec{k}_{\parallel}\cdot\vec{R}}$. Depending upon the value of $\vec{k}_{\parallel}$ (i.e., the angle of incidence, θ, and the azimuthal angle, ϕ, of the conduction-electron wave) this superposition may or may not contain a constructive interference term corresponding to a diffracted wave. To see this explicitly we may use Eq. (35) and exclude the term at the origin to form S' as

$$S' = \frac{2\pi i}{A} \sum_{\vec{g}} \left(\frac{1 - e^{2iK_{\vec{g}} d}}{K_{\vec{g}}} \right) - \lim_{R \to 0} \frac{e^{ikR}}{R} + \frac{e^{2ikd}}{2d} \; . \tag{48}$$

At first sight, it may appear that S', in the form of Eq. (48), diverges due to the singular term $\lim_{R \to 0} e^{ikR}/R$. However, the singularity is cancelled by the sum $\sum_{\vec{g}} (1/K_{\vec{g}})$ which is also singular. Because of this property, Eq. (48) is not useful in calculating the sum S_1', for which we used the Ewald technique. But Eq. (48) does serve to point out the difference in behavior of S' in the diffraction and nondiffraction cases.

Consider the imaginary part of S'. When a diffracted wave occurs, this is

$$\mathrm{Im} S' = \frac{4\pi}{A} \frac{\sin^2 k_x d}{k_x} + \frac{4\pi}{A} \frac{\sin^2 K_1 d}{K_1} - k + \frac{\sin 2kd}{2d} \; . \tag{49}$$

For the case of no diffraction, this is

$$\mathrm{Im} S' = \frac{4\pi}{A} \frac{\sin^2 k_x d}{k_x} - k + \frac{\sin 2kd}{2d} \; . \tag{50}$$

The above discussion shows that the sum S' has markedly different behavior depending upon whether or not a surface diffracted wave is present. This behavior is monitored by the factor $1/\{1 - c[\tilde{t}(k)/\alpha]S'\}$ and accordingly yields a different effective distorted wave incident at a coherent potential scattering center for the two situations. In this way, the resonance in the specular probability is produced.

For a given concentration of adsorbate, the characterization of the resonance as a dent or a bump (or both) in the specular probability curve depends upon the values of the scattering parameter $\tilde{t}(k)$ of the adsorbed impurity, the Fermi wave vector, k, and the surface lattice parameter, a. This dependence occurs in a complicated manner.

In general, however, the resonance effect is greater for higher concentrations of adsorbate since the multiple-scattering factor $1/\{1 - c[\tilde{t}(k)/\alpha]S'\}$ changes more significantly as the diffracting mode is transformed to the nondiffracting mode (i.e., as the angle of incidence passes the resonance angle). This is illustrated in Figs. 5 and 6.

Note that while the specular probability, P_s, is always a continuous, smooth function of θ, the conduction-electron probability of nondiffuse scattering, P_{nd}, suffers a discontinuity at the resonance angle (reflecting the cutoff of the extra diffracted wave that occurs there).

For completeness, we mention two properties that Figs. 3 and 4 also demonstrate in addition to the resonance effect. These are general properties that are, in fact, present in all curves of P_s vs θ given in this work. First of all, at glancing incidence, the specular probability is always unity. This is in agreement with physical intuition (i.e., thinking of electron waves as similar to light waves reflected from a surface), the Greene theories and also magnetic surface state experiments.[32–34] Second, at normal incidence, the specular probability always has zero slope. This follows from the equivalence (from symmetry) of incidence of the electron wave on either side of the normal to the averaged surface. Thus, the specular probability is an even function of the angle $(90° - \theta)$ and gives a zero slope at $\theta = 90°$.

B. Multiple scattering versus single scattering

The difference in the specular probability as obtained from either the multiple-scattering calculation [Eq. (40)] or the single-scattering calculation [Eq. (40) with $S' = 0$] is shown in Figs. 5 and 6.

For low concentrations of adsorbate the two theories are in close agreement, as we expect. For higher concentrations, however, the single-scattering result deviates significantly from the multiple-scattering result, as Fig. 5 demonstrates. This is particularly true in the case where resonance occurs since the resonance effect is not predicted by the single-scattering theory.

At concentrations of adsorbate approaching full coverage of the surface the two calculations are in strong disagreement. The multiple-scattering theory contains a modification of the effective distorted wave incident at a surface scatterer that is a function of the concentration. Figure 6 demonstrates that in the absence of this modifying influence, the predicted specular probability may be in obvious error. For high concentrations, the single-scattering theory may yield a specular probability greater than unity. This unwelcome feature is, in fact, contained in the single-scattering Greene theories.[6]

C. Nordheim dependence of the diffuse probability on the concentration

In our model, which contains the simplifying assumptions of an uncorrelated surface impurity and a smooth, nonreconstructed metal surface, we expect that the electron probability of diffuse surface scattering, P_d, should *vanish* for a perfectly ordered surface (i.e., one with either no adsorbate or a full monolayer of adsorbate). Experimental data on resistivity of thin metal films measured as a function of concentration of adsorbate has been obtained by Lucas[35] for gold atoms adsorbed onto a presumably specular gold surface and by Geus[1] for hydrogen molecules adsorbed onto an iron surface. Both of these experiments reflect the above mentioned expectation as an initial increase in resistivity (more diffuse scattering) as the clean surface begins to be contaminated followed by a decrease in resistivity (less diffuse scattering) as the contamination approaches full coverage. Note, however, that other experiments[1] measuring film resistivity versus adsorbate concentration for different adsorbate and metal surface contaminations do not yield this behavior. This may be attributable to the formation of complicated surface compounds (which may depend on the pressure, temperature and even the concentration of adsorbate), the formation of superlattices, or the *absorption* of the impurity atoms. Recently, however Pariset and Chauvineau,[12] for the case of iron atoms adsorbed onto gold films, have obtained a maximum of resistivity in the vicinity of half a monolayer of coverage. Furthermore, they have effectively argued that this behavior is attributable to an increase in the diffuse surface scattering of the conduction electrons, since surface compound formation and absorption of the impurity atoms has been shown, in this case, to proceed only after the formation of a monolayer of adsorbate.

Here we show that the multiple-scattering theory yields the expected decrease in P_d as the surface becomes more ordered. In particular, we find that P_d has a $c(1-c)$ dependence on the concentration. This is analogous to the well-known Nordheim approximation[36] in the theory of bulk electron scattering in substitutionally disordered alloys.

The diffuse probability, for the general case where a specular and diffracted wave is present, is given by

$$P_d = 1 - |R_{\bar{\vec{k}}}|^2 - \frac{K_1}{k_x}|R_{\vec{K}_1}|^2 \ .$$

Using Eqs. (40) and (41), we obtain

$$P_d = \left[\frac{16\pi}{A}\left(\frac{\sin^2 k_x d}{k_x}\right) c \left(\mathrm{Im}\frac{\tilde{t}(k)}{\alpha} + c\left|\frac{\tilde{t}(k)}{\alpha}\right|^2 \mathrm{Im}S' \right) \right.$$
$$\left. - \frac{64\pi^2}{A^2}\left(\frac{\sin^2 k_x d}{k_x}\right) c^2 \left|\frac{\tilde{t}(k)}{\alpha}\right|^2 \left(\frac{\sin^2 k_x d}{k_x} + \frac{\sin^2 K_1 d}{K_1}\right) \right] \Big/ \left|1 - c\frac{\tilde{t}(k)}{\alpha}S'\right|^2 \ .$$

Substituting for ImS' from Eq. (49) gives

$$P_d = \frac{\dfrac{16\pi}{A}\dfrac{\sin^2 k_x d}{k_x}\left[c\,\mathrm{Im}\left(\dfrac{\tilde{t}(k)}{\alpha}\right) + c^2\left|\dfrac{\tilde{t}(k)}{\alpha}\right|^2 \left(\dfrac{\sin 2kd}{2d} - k\right)\right]}{\left|1 - c\dfrac{\tilde{t}(k)}{\alpha}S'\right|^2} \ .$$

The definition of $\tilde{t}(k)$ [Eq. (11)] combined with the equation $\mathrm{Im} f_k = k\,|f_k|^2$ (i.e., the optical theorem) yields

$$\mathrm{Im}\left(\frac{\tilde{t}(k)}{\alpha}\right) = \left|\frac{\tilde{t}(k)}{\alpha}\right|^2 k \left(1 - \frac{\sin 2kd}{2kd}\right) \ ;$$

thus

$$P_d = \frac{\dfrac{16\pi}{A}c(1-c)\left(\dfrac{\sin^2 k_x d}{k_x}\right)\left|\dfrac{t(k)}{\alpha}\right|^2 \left(k - \dfrac{\sin 2kd}{2d}\right)}{\left|1 - c\dfrac{\tilde{t}(k)}{\alpha}S'\right|^2} \ . \tag{51}$$

Equation (51) exhibits the Nordheim property for conduction-electron scattering by the contaminated surface. It describes both the cases where a diffracted wave may arise (assumed above) and where only a specularly reflected wave is present. The different angle dependence in these cases occurs through the factor S'.

Note that the multiple-scattering parameter, ImS', provided the cancellation of terms that produced the $c(1-c)$ dependence. This result is not obtained in the single-scattering theory.

Figure 7 illustrates the Nordheim property for the situation where no diffraction occurs. Here the specular probability is closest to unity for the lowest and highest concentrations of adsorbate.

VI. SUMMARY AND CONCLUSIONS

We have examined the probabilities for specular reflection and diffraction of conduction electrons due to contamination at a smooth metal surface. Our most striking result has been to show that inclusion of multiple scattering between adsorbed impurities yields an unanticipated resonance effect in the specular probability that is associated with the occurrence of a surface diffracted electron wave. Although the diffracted wave occurs for angles close to glancing incidence, its scattering amplitude is small at such angles and vanishes for glancing incidence. Thus the presence of a diffracted wave at small angles is not in disagreement with previous theoretical[4–6,37] and experimental[32–34,38] results that show that the specular probability approaches unity as the electron strikes the surface at angles approaching glancing incidence.

We have also shown how a multiple-scattering calculation and the inclusion of evanescent waves at the surface modulates the effective wave incident at a surface scattering site so that the specular probability never exceeds unity and tends to its lowest value when the surface is most disordered (when the contamination approaches half coverage) in agreement with experiment.[1,12,35] As noted by Greene and Malamus[6] and Greene and O'Donnell,[5] their single-scattering theories break down in this regard (for high concentrations of adsorbate) essentially because of their use of the Born approximation, which neglects multiple scattering. Similarly, our own single-scattering calculation, used for comparison, has been shown to break down for high concentrations of adsorbate.

ACKNOWLEDGMENT

I wish to thank R. M. More for valuable discussions concerning much of this work.

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