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Surface high-energy electron diffraction

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High-energy (100-keV) grazing-incidence electron diffraction is proposed and analyzed as a technique for determining quantitatively the structure of surfaces. It is shown that, under suitable conditions, the Bragg scattering from the surface may be interpreted in terms of weak-scattering theory and a known electrostatic potential for the interaction of high-energy electrons with core electrons.

Electron diffraction from solid single-crystal surfaces is one of the best ways of obtaining information about the structure of such surfaces.[1] Typically, low-energy electrons ($E < 100$ eV) are used in such experiments. Quantitative interpretation of the data, for example, an analysis of the relative intensity in various Bragg spots or the energy dependence of a single spot, are extraordinarily difficult.[1,2] On the one hand, the electrons interact strongly with the solid so that the reflection coefficient even within a one-body approximation is the solution of a complicated multiple-scattering problem which for semiconductors is even more complicated by surface reconstruction, i.e., the unknown geometry of the surface. On the other hand, if one knows the effective one-electron potential, then one could, at least in principle, extract the surface geometry.

Determining such a potential (if it exists) has its own enormous problems since inherently the problem involves the interaction of 10^{23} identical electrons. The interaction between probe and system arises from an electrostatic Hartree piece dependent only on the ground-state charge distribution and an exchange and correlation part determined by some approximate technique. Typically, one makes some type of local-density approximation where the potential for electrons of energy E is given by $V_{\text{eff}}(r)=\Sigma(E,\rho(r))$, where Σ is the self-energy of an electron in a uniform electron gas with density $\rho(r)$ determined from a one-electron self-consistent ground-state calculation.[3] While such approximations seem to be adequate for describing many of the ground-state properties of solids,[4] it is not at all obvious that they are accurate for electrons with tens of eV of kinetic energy. Moreover, there is no *a priori* way of checking such approximations.

In this paper, we will show that an electron scattering experiment utilizing high-energy (100-keV) electrons incident at small angles on a clean single-crystal surface can be an almost ideal (known potential) kinematic probe of surfaces.[5] We will be able to argue that, under conditions easily attainable in a conventional electron microscope, it should be possible to perform these measurements. While such experiments [so-called reflection high-energy electron diffraction (RHEED)] have been carried out with roughly this geometry,[6] we know of no experiments where conditions were correctly optimized and analyzed to allow such a simple interpretation.[7] It is true, however, that in Ref. 7 an empirical rule, relating the intensities of the bulk peaks to the surface peaks formed by adsorbing oxygen on tungsten, was used to define a weak-scattering regime. *A posteriori* it may be said that this procedure worked, i.e., there was good agreement between experimentally measured and kinematically calculated intensities. This work in fact tells us that there is indeed a regime where such simple calculations may apply.

For the moment, let us assume that the solid is made up of an array of atoms centered at R_i each with its own ground-state charge distribution $\rho(r'-R_i)$. This is an excellent approximation for the core electrons and we will see that, in these experiments, it is the core electrons which are relevant. The scattering of a 100-keV electron by an atom is very accurately described by Born approximation from the ground-state charge distribution (no correlation, no exchange); i.e.,

$$\frac{d\sigma}{d\Omega} = |f_i(\theta)|^2 \tag{1}$$

with ($\hbar=1$)

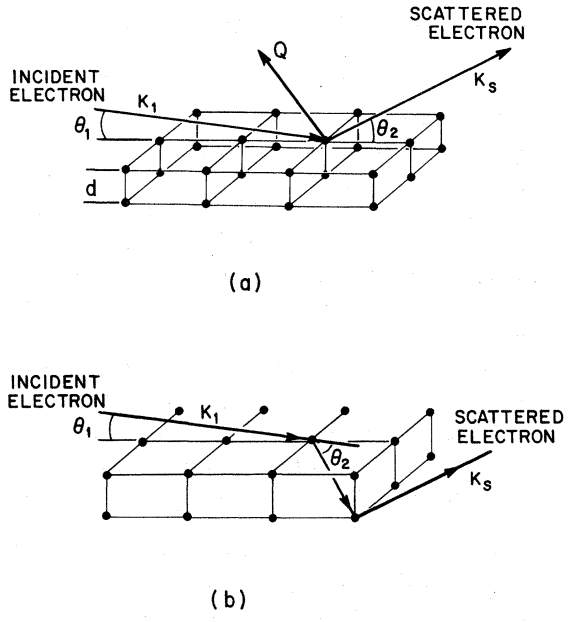

FIG. 1. (a) Schematic representation of the single scattering of high-energy electrons from the surface of a simple cubic lattice ($\theta_1 \approx 10^{-3}$ rad, $\theta_2 \approx 10^{-1}$ rad). (b) A typical multiple-scattering event.

$$f_i(\theta) = -\frac{m}{2\pi} \int V_i(r) e^{i\vec{k}\cdot\vec{r}} d^3r \ . \tag{2}$$

Here

$$V_i(r) = \frac{Ze^2}{|r-R_i|} - \int \frac{\rho(r'-R_i)d^3r'}{|r-r'|} \tag{3}$$

and k is the momentum transferred in the scattering. To obtain the qualitative behavior of the cross sections, we assume a hydrogenic charge distribution of the form $\rho(r) \sim e^{-r/a_l}$ in the lth shell containing n_l electrons. The integrals are easily done,

$$f_i(\theta) = -\frac{2m}{\pi} \left[\frac{Ze^2}{k^2} - \frac{n_l e^2}{k^2} \frac{1}{(1+k^2 a_l^2)^2} \right] e^{i\vec{k}\cdot\vec{R}_i} \ . \tag{4}$$

At small momentum transfers, the k^2 divergence vanishes since $\sum_l n_l = Z$. At large k, the scattering is dominated by the pointlike nucleus and those shells with the smallest a_l. Thus for $k \cong 10$ Å^{-1}, only those shells whose radii are, roughly speaking, 0.1 Å, i.e., bound by several hundred volts, will contribute. The typical size of the cross section at a momentum transfer $k \cong 10^9$ cm^{-1} is

$$\left[\frac{d\sigma}{d\Omega}\right]_T \cong \left[\frac{e^2 Z' m}{2k^2}\right]^2 \cong Z'^2 10^{-19} \tag{5}$$

in units of cm^2. The quantity Z' will depend on the details of the core charge distribution, but for a semiconductor like silicon, at these momentum transfers, $Z' \cong 3$ and $(d\sigma/d\Omega)_T \cong 10^{-18}$ cm^2.

Now consider the scattering of a beam of 100-keV electrons from the surface of a bulk single crystal as shown in Fig. 1(a). If the angle θ_1 is small enough, then the angle inside the crystal will be determined by the normal kinetic energy gained (ΔE) by the electron on entering the crystal. For $\theta < \sqrt{\Delta E/E}$, $\theta_{\rm int} \cong \sqrt{\Delta E/E} \cong 2 \times 10^{-3}$ for $E = 100$ keV since $\Delta E \sim 10$ eV. In this case the effective distance between planes $l_1 \cong d/\theta_{\rm int} \cong 1.5 \times 10^3$ Å. The distance l_1 will be comparable to the mean free path (λ_T) for inelastic scattering. For Si, $\lambda_T \cong 800$ Å for 100-keV electrons.[8] Thus the straight-through beam will, with 70% certainty, have suffered an inelastic scattering. This inelastic event will be dominated by forward plasmon scattering so that an energy analysis (with 10-eV resolution) of the final beam will eliminate much of the multiple scattering from the underlying bulk atoms.

While energy analysis eliminates some multiple scattering from the straight-through beam, there can, of course, be events like those sketched in Fig. 1(b) where diffuse scattering deflects the beam through some modest angle $\theta_D >> \theta_{\rm int}$. That beam may be diffusely scattered or diffracted into the final-beam direction. Each such scattering event involves momentum transfers of several Å^{-1} and the cross sections for these processes ($\sigma \cong 10^{-17} - 10^{-18}$ cm^2) are such that a single plane of atoms containing 10^{15} atoms/cm^2 is a weak scatterer. Such events will produce a background *comparable* to the diffraction peak from a single layer, but they are not localized in angle, i.e., they should be easy to subtract out. This is very different from the situation which prevails in inelastic scattering experiments, particularly as regards the behavior of the plasmon at large momentum transfers.[9] In this case, the plasmon cross section gets very large in the forward direction, i.e., for small momentum transfers it diverges logarithmically, so that background events involving a diffuse scattering followed by a forward inelastic scattering from the conduction electrons swamp the single-scattering event. In addition, unlike the elastic peak, the single-scattering event becomes broad in energy space and is almost impossible to

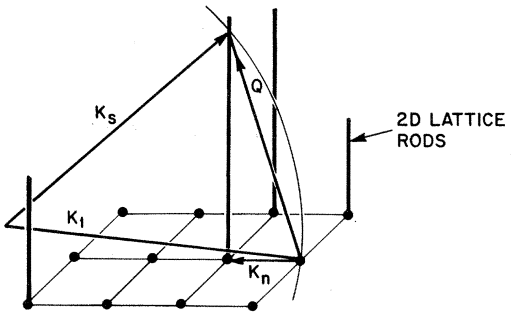

FIG. 2. The kinematics of the surface scattering. The three-dimensional Bragg points have been spread into the two-dimensional lattice rods.

distinguish from the multiple-scattering background.

The kinematics of the scattering process from the first layer is sketched in Fig. 2. Since it is possible to pick up an arbitrary amount of momentum in the z direction, the Bragg spots become Bragg rods. For a fixed input angle, the diffracted beam exits in a number of spots determined by that input angle and the momentum transfer in the plane, i.e., it is the place where the Bragg rods intersect the Ewald sphere. For such small incident angles, the diffracted beam makes an angle

$$\theta_2 \cong \sqrt{2K_n/k_1} \cong 10^{-1} , \tag{6}$$

measured in radians. Here K_n is some two-dimensional reciprocal-lattice vector taken, for convenience, in the x direction and $k_1 \cong 100$ Å^{-1} for a 100-keV electron. This implies that the *net* momentum transfer involved in the elastic scattering is approximately 10 Å^{-1} and that the Born approximation for scattering from atoms in the first plane is a very good approximation.

Due to scattering from the first layer, the fractional intensity in each singly diffracted beam is[10]

$$\frac{I_n}{I_0} \cong n \left[\frac{d\sigma}{d\Omega} \right]_T \cong 10^{-3} - 10^{-4} . \tag{7}$$

Here, n is the number of scatterers per unit area and $(d\sigma/d\Omega)_T$ is the typical cross section [Eq. (5)] characteristic of momentum transfers $k \cong 10$ Å^{-1}. Assuming the background is low enough, these numbers are exceptionally favorable. The background events will be dominated by inelastic scattering from the outer electrons and from quasielastic scattering, as discussed, from phonons. Compton-type events involving momentum transfers $k \cong 10$ Å^{-1} involve energy losses of several hundred electron volts ($\hbar^2 k^2/2m = 400$ eV, $k = 10$ Å^{-1}) and can be discriminated against by energy analyzing the scattered beam. As discussed, the diffuse background is broad and weak.

There is another type of elastic multiple scattering which could confuse any simple interpretation of the data. These are multiple-scattering events from the first plane of atoms involving small (several Å^{-1}) momentum transfers (K_n) perpendicular to the scattering plane. However, since the typical cross sections make a single plane of atoms a weak scatterer ($\approx 10\%$), even for low momentum transfers such events will only produce corrections to the intensity of approximately 1%. Such complications may be further suppressed by orienting the two-dimensional surface relative to the scattering plane such that there are no lower-order reciprocal-lattice vectors exactly perpendicular to the scattering plane. In this case, because of kinematic restrictions, the total momentum transfers [see Eq. (6)] are large and the cross section is even smaller. This situation is to be contrasted with the low-energy electron case where a single plane of atoms is a strong scatterer.

We envisage first measuring the relative intensity in $3N$ (N being the number of atoms in a unit cell) spots for a very small θ_1. These results can be analyzed in terms of the known form factors $F(k_n)$ (Born approximation, atomic charge distribution) to obtain the positions of the atoms in the first layer. We have

$$F(k_n) = \left| \sum_{i=1}^{N} e^{i\vec{k}_n \cdot \vec{r}_i} f_i(k_n) \right|^2 \tag{8}$$

with (in Hartree-Fock approximation)

$$f_i(k) \sim \sum_l \int e^{i\vec{k}\cdot\vec{r}} \phi_{il}^2(r) d^3r . \tag{9}$$

Here, the sum on i is a sum over the unit cell for the first layer of atoms and the sum on l is over occupied orbitals for the ith atom.

One can now repeat the process for a bigger incident angle and begin to observe the modulation in intensity of some particular Bragg spot (rod) which comes about as the interference between the first and second layers starts to become important. This should enable one to get a great deal of additional information about the nature of reconstruction (if it exists) as a function of distance into the sample.

There is another interesting related phenomenon which comes into play here. It is the "analog" of total external reflection in the x-ray case.[11] The

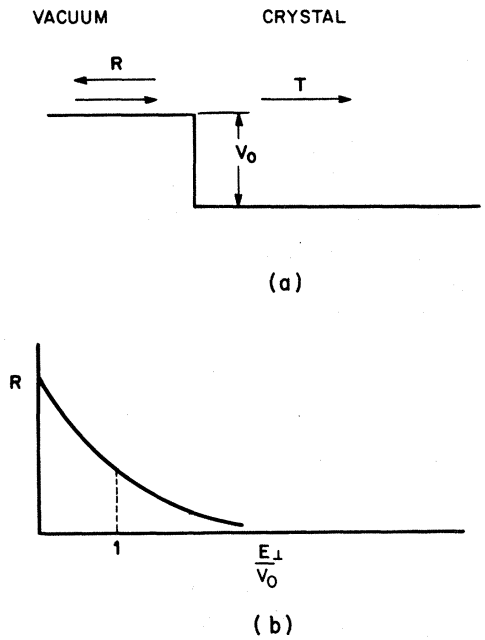

FIG. 3. (a) The effective barrier (electrostatic) seen by an incoming electron with high parallel energy and low longitudinal energy. (b) The reflection coefficient for the same electron.

normal energy of the electron is low and becomes of order of 1 eV for $\theta_i \cong 3\times 10^{-3}$ rad. The normal potential energy experienced by such an electron is very roughly sketched in Fig. 3. The height of this potential step "to a very high degree of accuracy" is given by the electrostatic potential difference V_0 ($V_0 \cong 10$ eV). Correlation and exchange effects are absent because of the very large parallel energy. In this case, the reflection coefficient goes to unity at zero energy. For a square well, the exact way it approaches one is given by

$$R = 1 - 4\sqrt{E_\perp / V_0} + \cdots , \tag{10}$$

where $E_\perp$ is the perpendicular energy ($E_\perp / E << 1$). Thus a measurement of the inital deviation of the reflection coefficient from one [Fig. 3(b)] will give the parameter V_0. Higher corrections in E will tell us about the detailed shape of the potential.[12]

In summary, then, we have argued that for sufficiently small angles of incidence, high-energy electron diffraction can be made extremely sensitive to the first layer. In addition, the potential between probe and substrate is known, and for some spots (rods) and for some geometric configurations, the intensity can be interpreted simply within the Born approximation. There will no doubt be real practical problems connected with flatness of the crystal, the brightness of the source, etc. We have considered all of these questions in some detail and find that they can all be solved in a conventional electron microscope which has been adapted to work at UHV.

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