Angle-Resolved Electron-Energy-Loss Spectroscopy: Atomic-Core Excitations at Adsorbates on Surfaces

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By treatment of the incident and detected electron states in a LEED formalism, it is shown that the dominant processes contributing to a surface electron-energy-loss fine-structure (SEELFS) spectrum from atomic adsorbates on crystal surfaces are those involving elastic backscattering and small-angle inelastic scattering. This justifies the use of the "dipole approximation" for the atomic matrix elements in the interpretation of SEELFS. The angular dependence of the detected electrons is calculated for the first time and its potential for surface structure determination discussed.

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The study of surface electron-energy-loss fine structure (SEELFS)[1] offers essentially the same local surface structural information as that provided by surface extended x-ray-absorption fine structure (SEXAFS).[2-4] However, the need for only such common laboratory-based equipment as an electron gun rather than a central radiation source such as a synchrotron, as is the case with SEXAFS, enables SEELFS to be much more accessible to surface science laboratories. The main price to be paid is a more complex theory, due to the much stronger elastic scattering of the incident electron beam, and due to the effects of exchange between the projectile and localized electrons. The first serious attempt at such a theory was that of Mila and Noguera[5] who treated the exchange and the elastic scattering of the higher-energy electrons in a single-scattering photoelectron diffraction[6-8] formulation. Treating the case of core-electron excitations from atomic adsorbates on surfaces, I present here what I believe to be a more complete theory which treats the full multiple scattering of the projectiles both *before* and *after* the inelastic scattering in a low-energy electron diffraction (LEED) formalism.[9,10] This makes possible a convenient classification of the electron-scattering paths, from which it becomes clear that the dominant ones involve elastic backscattering and small-angle inelastic scattering, which offers an explanation for the apparent dominance of the "dipole" selection rule in the atomic excitation processes.[11] The angular dependence of electrons after energy loss due to the excitation of atomic-core electrons from disordered adsorbates on crystal surfaces is calculated for the first time and its potential for surface structure determination discussed.[12]

An incident electron of energy E_0 can interact with an atomic-core electron of energy E_b via a Coulomb mechanism to generate a final state in which the electrons have energies E_f and E_x. Energy conservation requires that

$$E_0+E_b=E_f+E_x. \tag{1}$$

With allowance for exchange, the initial and final wave functions of the two-electron system can be represented by

$$\{\exp(i\mathbf{K}\cdot\mathbf{r}_1)\Phi_c(\mathbf{r}_2)\pm\exp(i\mathbf{K}\cdot\mathbf{r}_2)\Phi_c(\mathbf{r}_1)\}/\sqrt{2} \tag{2}$$

and

$$\{\exp(i\mathbf{K}'\cdot\mathbf{r}_1)\Phi_x(\mathbf{r}_2)\pm\exp(i\mathbf{K}'\cdot\mathbf{r}_2)\Phi_x(\mathbf{r}_1)\}/\sqrt{2}, \tag{3}$$

respectively, where the incident and detected electrons are taken to be plane waves of wave vectors $\mathbf{K}$ and $\mathbf{K}'$ and energies E_0 and E_f, respectively. The initial core wave function is Φ_c, the final-state core wave function of lower energy E_x is Φ_x, and $\mathbf{r}_1$ and $\mathbf{r}_2$ are the position vectors of the two electrons. The positive sign is operative in the triplet case of parallel electron spins and the negative sign in the singlet case of antiparallel spins. If we take a Coulomb interaction between the two electrons of the form

$$T=e^2/4\pi\epsilon_0|\mathbf{r}_1-\mathbf{r}_2|, \tag{4}$$

it can be shown[13] that the matrix element for the transition is

$$(1/Q^2\pm 1/K^2)M(\mathbf{Q}), \tag{5}$$

where

$$M(\mathbf{Q})=\left\{\int\Phi_x^*(\mathbf{r})\exp(i\mathbf{Q}\cdot\mathbf{r})\Phi_c(\mathbf{r})d\mathbf{r}\right\}e^2/\epsilon_0 \tag{6}$$

and

$$\mathbf{Q}=\mathbf{K}-\mathbf{K}'. \tag{7}$$

Consider an experiment performed on a sample consisting of a disordered atomic adsorbate on a crystal surface. Diffraction of the incident and detected electrons by the substrate can be taken into account by the representation of them by LEED states

$$\langle \mathbf{r} \,|\, \mathbf{K}_\parallel, E_0 \rangle = \exp\{i\mathbf{K}_0^{+} \cdot (\mathbf{r}-\mathbf{r}_0)\} + \textstyle\sum_{\mathbf{g}} R_{\mathbf{g}0}(E_0, \mathbf{K}_\parallel) \exp\{i\mathbf{K}_{\mathbf{g}}^{-} \cdot (\mathbf{r}-\mathbf{r}_0)\}, \tag{8}$$

$$\langle \mathbf{r} \,|\, \mathbf{K}'_\parallel, E_f \rangle = \exp\{i\mathbf{K}_0'^{+} \cdot (\mathbf{r}-\mathbf{r}_0)\} + \textstyle\sum_{\mathbf{g}'} R_{\mathbf{g}'0}(E_f, \mathbf{K}'_\parallel) \exp\{i\mathbf{K}_{\mathbf{g}'}'^{-} \cdot (\mathbf{r}-\mathbf{r}_0)\}, \tag{9}$$

respectively, characterized by energies E_0 and E_f and wave-vector components $\mathbf{K}_\parallel$ and $\mathbf{K}'_\parallel$ parallel to the surface. $R_{\mathbf{gg}'}$ are elements of LEED reflection matrices of the substrate defined with respect to an origin represented by $\mathbf{r}_0$, which can be calculated by the standard techniques of LEED theory,[9,10] where $\mathbf{g}$ and $\mathbf{g}'$ are reciprocal-lattice vectors of the substrate and

$$\mathbf{K}_{\mathbf{g}}^{\pm} = (\mathbf{K}_\parallel + \mathbf{g}, K_{\mathbf{g}z}^{\pm}) \tag{10}$$

with

$$K_{\mathbf{g}z}^{\pm} = \pm [2E_0 - (\mathbf{K}_\parallel + \mathbf{g})^2]^{1/2}, \tag{11}$$

and

$$\mathbf{K}_{\mathbf{g}'}'^{\pm} = (\mathbf{K}'_\parallel + \mathbf{g}', \mathbf{K}_{g'z}'^{\pm}) \tag{12}$$

with

$$K_{\mathbf{g}'z}'^{\pm} = \pm [2E_f - (\mathbf{K}'_\parallel + \mathbf{g}')^2]^{1/2}. \tag{13}$$

The matrix element for the transition between the states (8) and (9) accompanying the excitation of a core electron of the adsorbate,

$$\langle E_f, \mathbf{K}'_\parallel; \Phi_x \,|\, T \,|\, \Phi_c; \mathbf{K}_\parallel, E_0 \rangle, \tag{14}$$

can be written

$$A(E_0, \mathbf{K}_\parallel; E_f, \mathbf{K}'_\parallel) = A_1 + A_2 + A_3 + A_4, \tag{15}$$

where

$$A_1 = M(\mathbf{Q}_{00}^{++}) D_{00}^{++} \exp\{i\mathbf{Q}_{00}^{++} \cdot (\mathbf{r}_a - \mathbf{r}_0)\}, \tag{16}$$

$$A_2 = \textstyle\sum_{\mathbf{g}'} M(\mathbf{Q}_{0\mathbf{g}'}^{+-}) D_{0\mathbf{g}'}^{+-} R'_{\mathbf{g}'0}(E_f, \mathbf{K}'_\parallel) \exp\{i\mathbf{Q}_{0\mathbf{g}'}^{+-} \cdot (\mathbf{r}_a - \mathbf{r}_0)\}, \tag{17}$$

$$A_3 = \textstyle\sum_{\mathbf{g}} M(\mathbf{Q}_{0\mathbf{g}}^{+-}) D_{0\mathbf{g}}^{+-} R_{\mathbf{g}0}(E_0, \mathbf{K}_\parallel) \exp\{i\mathbf{Q}_{0\mathbf{g}}^{+-} \cdot (\mathbf{r}_a - \mathbf{r}_0)\}, \tag{18}$$

$$A_4 = \textstyle\sum_{\mathbf{gg}'} M(\mathbf{Q}_{\mathbf{gg}'}^{--}) D_{\mathbf{gg}'}^{--} R_{\mathbf{g}0}(E_0, \mathbf{K}_\parallel) R_{\mathbf{g}'0}(E_f, \mathbf{K}'_\parallel) \exp\{i\mathbf{Q}_{\mathbf{gg}'} \cdot (\mathbf{r}_a - \mathbf{r}_0)\}, \tag{19}$$

$$D_{\mathbf{gg}'}^{\pm\pm} = 1/(Q_{\mathbf{gg}'}^{\pm\pm})^2 \pm 1/2E_0, \tag{20}$$

$$\mathbf{Q}_{\mathbf{gg}'}^{\pm\pm} = \mathbf{k}_{\mathbf{g}}^{\pm} + \mathbf{K}_{\mathbf{g}'}^{\pm\prime}, \tag{21}$$

where $\mathbf{r}_a$ specifies the position of the adsorbate.

The intensity measured by a small-angle electron energy analyzer can be evaluated from

$$I(E_f, \mathbf{K}'_\parallel; E_0, \mathbf{K}_\parallel) = |A(E_f, \mathbf{K}'_\parallel; E_0, \mathbf{K}_\parallel)|^2 K'_{0z}/K_{0z}. \tag{22}$$

The physical significance of the terms A_1 to A_4 is illustrated in Fig. 1. The geometry of the experiment[1] requires that the detected electrons be propagating in a direction almost opposite to that of the incident beam. The signal therefore involves not only an inelastic scattering of the incident beam at the adsorbate, but also some form of backscattering process. In (16) to (19) the inelastic scattering is represented by the products of the factors M and D, while the remaining factors represent elastic backscattering by the substrate. A_1 describes inelastic backscattering at the adsorbate, A_2 (nearly) forward inelastic scattering by the adsorbate followed by elastic (LEED) backscattering from the substrate, A_3 the processes of A_2 in reverse order, and A_4 two LEED backscattering processes sandwiching an inelastic backscattering.

The decomposition of the scattering paths in this fashion enables us to identify the most significant terms contributing to the signal. At LEED energies (~40 to 500 eV) or above, backscattering, elastic or inelastic, is much less likely than forward scattering. Whereas A_4 contains only terms involving at least three backscattering events, A_1, A_2, and A_3 include terms involving only one such event. Therefore A_4 can be neglected without

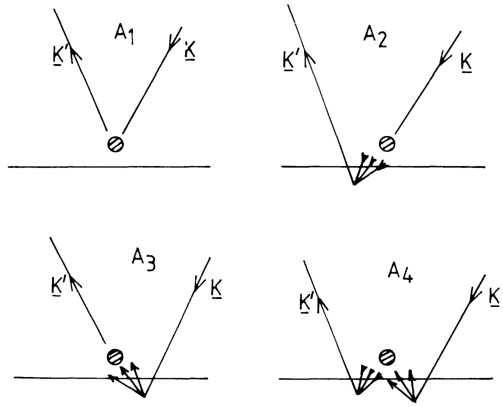

FIG. 1. Schematic representation of the scattering paths described by terms A_1 to A_4. The hatched circle represents an adsorbate atom on a crystal surface.

any significant loss of accuracy. The relative importance of the other terms depends on the relative magnitudes of elastic and inelastic backscattering. On the assumption that the terms M in (16) to (18) are of the same order of magnitude, we need only examine the relative magnitudes of the terms D and R.

If the magnitude of the energy loss $\Delta E(=E_0-E_f)$ is much smaller than E_0 then the following order-of-magnitude estimates apply:

$$|D_{00}^{++}| \simeq 1/2E_0, \tag{23}$$

where the exchange term $\pm 1/2E_0$ is the main contributor. For the dominant terms in the sums (17) and (18), we have

$$|D_{\mathbf{gg}'}^{+-}| \simeq 2E_0/(\Delta E)^2, \tag{24}$$

where the exchange term is negligible. Then we see that A_1 will be negligible compared with A_2 and A_3 if

$$|D_{00}^{++}| \ll |D_{\mathbf{gg}'}^{+-}|R, \tag{25}$$

i.e.,

$$\Delta E/E_0 \ll 2\sqrt{R}, \tag{26}$$

where R is the magnitude of a typical LEED reflection matrix element. Given that a typical reflection intensity is about 10^{-2} of the incident-beam intensity even at the high end of the LEED range, which overlaps with the SEELFS range ($\simeq$500 eV to 2.5 keV),[11] the term on the right-hand side of (26) is about unity and it would be expected that provided

$$\Delta E/E_0 \ll 1, \tag{27}$$

A_1 would be negligible compared with A_2 or A_3. The latter quantities, however, are of comparable magnitude, emphasizing the necessity of the consideration of the elastic scattering of the incident electrons *before* the inelastic process.

Note also (see, e.g., Fig. 1) that A_1 and A_4 involve inelastic *backscattering* with a large $Q \sim 2(2E_0)^{1/2}$, while A_2 and A_3 are dominated by *small-angle* inelastic scattering for which $Q \sim \Delta E(2E_0)^{-1/2}$. If we take $r_c \sim a_0/Z$ as the extent of an inner shell in an atom of atomic number Z (where a_0 is the Bohr radius), it is readily seen that, if (26) holds, the condition

$$Qr_c \ll 1 \tag{28}$$

is valid for the dominant terms A_2 and A_3, but not for the negligible ones A_1 and A_4, in the SEELFS range of the energy E_0. But (28) is the very condition for the approximation of the SEELFS matrix element (6) by its SEXAFS counterpart

$$\int \Phi_x^*(\mathbf{r})\mathbf{Q}\cdot\mathbf{r}\Phi_c(\mathbf{r})d^3r, \tag{29}$$

where $\mathbf{Q}$ is reinterpreted as an electric-field vector, thus justifying the use of the dipole approximation for the matrix elements in the interpretation of SEELFS spectra.

The type of signal which could be expected from angle-resolved experiments is indicated by our considering a special case, namely that of a disordered layer of Na on Ni(100). In the ordered $c(2\times2)$ structure conventional LEED studies[14] have suggested that the Na atoms occupy the four-fold hollow sites, 2.3 Å from the Ni surface. Figure 2 indicates the polar-angle variation of the SEELFS signal along a [100] azimuth for an incident electron beam of energy 544 eV and a detected beam of 430 eV. The ionization energy of the Na L_{I} edge is 76 eV and therefore the detected beam corresponds to an energy about 38 eV above the absorption edge. Different heights of the Na atom above the surface are considered, and the strong variation of the signal is an encouraging indication of this technique as a surface structural probe. The importance of including the A_3 term is illustrated by the dashed curves, in which this term is omitted in the calculation.

The calculations were performed by modifications of programs developed for the calculation of diffuse LEED intensities.[15] For energy losses greater than about 20 eV

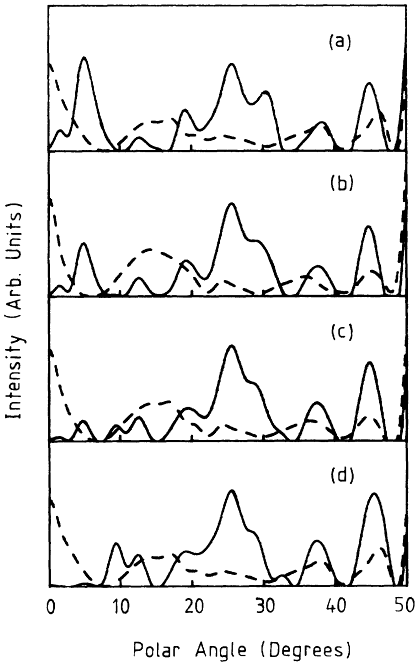

FIG. 2. Polar-angle variation of the reflected electron-energy-loss spectroscopy intensity expected from a [100] azimuth on disordered Na/Ni(100). Na L_{I}-shell excitation. $E_0=544$ eV, $E_f=430$ eV. Imaginary part of the optical potential, $v_{0i}=-4$ eV; 49 beams were used to represent the LEED states. Dashed curves indicate the effect of the A_2 term only. The full curve includes the interference between A_2 and A_3. Heights (d) of Na atoms from surface (hollow-site adsorption): (a) $d=2.6$ Å, (b) $d=2.5$ Å, (c) $d=2.4$ Å, and (d) $d=2.3$ Å.

the matrix elements (6) are dominated by a monotonically decreasing contribution due to an isolated atom. For excitations from spherically symmetric core wave functions this is independent of **Q**. To a very good approximation, therefore, the matrix elements need not be evaluated in the calculation of the angular dependence of the detected electrons.

The possibility of angle-resolved detection has already been demonstrated by Tyliszczak and Hitchcock,[16] who used a concentric hemispherical analyzer rather than the more conventional cylindrical mirror analyzer.[1] The information from the experiment can be multiplied many fold by our considering different azimuthal angles and different energies of the detected electrons. In this the technique has much in common with that of diffuse LEED.[15,17,18] One potential problem with that case is that anything (e.g., point defects, terminating dislocations, etc.) which breaks the periodicity of the surface may contribute to the signal. In the present technique, however, concentration on electrons of energies close to the absorption edges of the adsorbate ensures that signals originate from only the immediate vicinity of the adsorption site.

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