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Extended x-ray-absorption fine structure–Auger process for surface structure analysis: Theoretical considerations of a proposed experiment

(synchrotron spectroscopy)

UZI LANDMAN* AND DAVID L. ADAMS†

* Institute for Fundamental Studies, Department of Physics and Astronomy, University of Rochester, Rochester, New York 14627; and † Institute of Physics, Aarhus University, 8000 Aarhus C, Denmark

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ABSTRACT A method for surface structure analysis is proposed. The proposed process combines x-ray photoabsorption and Auger electron emission. The extended x-ray-absorption fine structure, occurring for photon energies above an atomic absorption edge, contains structural information of the microscopic environment due to the coupling of the photoelectron final state with the atomic initial state. Measurement of the variations in the intensity of particular Auger lines, as a function of the incident radiation energy, provides a surface sensitive measure of the photoabsorption cross section in the media. Theoretical considerations of the physical processes underlying the proposed experiment and its feasibility, and a discussion of background contributions are presented.

Structural information of matter is derived almost exclusively via diffraction phenomena (1, 2). Both electromagnetic radiation and particles are used, the basic requirement of the experiment being that the wavelength of the incident beam be of the same order as atomic distances in the system under study [i.e., for x-rays, neutrons, and electrons the wavelength is related to the energy, ϵ (in ev), as λ (Å) $\cong 12.4 \times 10^3/\epsilon$, $0.28/\epsilon^{1/2}$, and $12/\epsilon^{1/2}$, respectively]. It is only recently that the atomic absorption of x-rays has been recognized as a promising technique for structural studies[‡] (7–11). In the current theoretical model the fine structure in the absorption above the absorption edge [extended x-ray-absorption fine structure (EXAFS)] above about 50 ev from the edge, originates from the interference of the backscattered (by the surrounding atoms) photoelectron with the outgoing wavefront, in the vicinity of the ionized center. This interference modulates the probability for photoabsorption and yields an oscillatory component in the absorption coefficient when measured as a function of the energy of the incident x-ray photon. Since the phase difference between the backscattered photoelectron and the outgoing wave depends on the positions of the scatterers (also on their atomic scattering factors and vibronic characteristics), the above modulation contains structural information[§]. The advantages of the EXAFS technique are the relaxation of the requirement of long-range order, common to most diffraction methods, and the ability to "tune" to the environment of particular chemical constituents (via the incident radiation). The feasibility of extracting geometrical information from the EXAFS signal has been demonstrated via the use of direct, Fourier transform (7–10), and indirect, model calculation (12, 13), methods of analysis. In the early EXAFS experiments, conventional x-ray sources were used, necessitating long counting periods (days) with signal-to-noise ratios of about 3×10^2. A new era in EXAFS studies started with the advent of synchrotron radiation from a storage ring. The radiation intensity from this source is larger by a factor of 5×10^4 over conventional sources, providing a superior signal-to-noise ratio of about 10^4 and allowing complete spectral measurements over short periods (about 30 min), with an energy resolution of about 1 ev (11).

While presenting a potentially powerful method for structural studies, the EXAFS method provides information predominately about the atomic organization in the bulk of materials, due to the large penetration length of x-ray. The arrangement of atoms in the surface region of condensed matter is a basic ingredient in the understanding of surface phenomena and interactions. Several methods that probe the surface region have been proposed (14). The most developed technique for surface structural analysis is the diffraction of low-energy electrons (LEED) (0–500 ev) from solids, which was discovered by Davisson and Germer in 1927 (15). The analysis of the electron-diffracted intensities is a complicated problem and has been satisfactorily achieved to date only for a few simple systems (16). In any case, this method applies only to materials that exhibit long-range order, dictated by the LEED coherence length (about 10^2 Å). Surface sensitivity of physical probes can be achieved by: (*a*) limiting the penetration of the incident particle, and/or (*b*) detecting only those particles that originate at the surface region (small escape length) of the material. In this note we propose a variatian of the EXAFS method that would gain in surface sensitivity while preserving the attractive features of the technique. The proposed experiment combines x-ray photoabsorption with Auger electron emission. A schematic description of the process is given in Fig. 1. The rate of photoabsorption (Fig. 1a) is the structure-dependent step, while the Auger process (Fig. 1b) provides a measure of the efficiency of the photoabsorption event. The surface sensitivity of the total process derives from the short escape length of selected Auger electrons. In the next section we discuss first the EXAFS process followed by a discussion of the Auger process and other decay mechanisms.

THE EXAFS–AUGER PROCESS

EXAFS

The cross section of photoabsorption is given by the golden-rule formula, which, in the dipole approximation, is given as

$$P = (2\pi/\hbar)\sum_f |M_{fs}|^2 \delta(E_i + \hbar\omega - E_f), \quad [1a]$$

$$M_{fs} = \langle f | e\epsilon \cdot \mathbf{r} | i \rangle, \quad [1b]$$

Abbreviations: EXAFS, extended x-ray absorption fine structure; LEED, low energy electron diffraction.

‡ Although the phenomenon of extended x-ray-absorption fine structure (EXAFS) was known for a long time (3–6), it is only recently that its significance as a potential analytical tool has been conceived (7–11).

§ In a sense, the photoionized atom serves as an internal spherical-electron-source and a phase-detector.

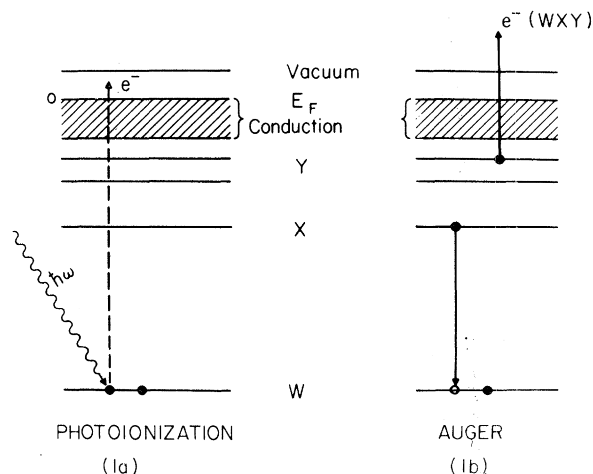

FIG. 1. Schematic description of the EXAFS–Auger process. Electronic energy levels (in a metal) are labeled by W, X, and Y, the conduction band is dashed, and the Fermi level is denoted by E_F. (a) The photoionization process: a photon of energy $\hbar\omega$ excites an electron (filled circle, dashed line) from the core-level W, leaving a hole in W. (b) The Auger process: an electron from level X fills the hole in level W, and an electron from level Y is emitted from the solid (leaving a doubly ionized atom), with a characteristic energy that depends on levels W, X, and Y.

where the initial state, i with energy E_i, consists of the atomic core and the Fermi sea, and the incident radiation field, the final state, f with energy E_f (larger than the Fermi level), consists of a core hole and an excited electron. ϵ is the polarization vector of the electric field, e the electron charge, and $\hbar\omega$ the x-ray photon energy. The major task in the evaluation of the cross section is the calculation of the wave function of the excited electron, i.e., the energy-conserving, attenuated propagation of the photoelectron in the medium. This problem is similar to the one encountered in LEED multiple-scattering calculations, with the differences being: (*a*) an additional shift of phase of the electron wave due to the influence of the central ionized atom and (*b*) the spherical symmetry of the outgoing electron wave. To treat (*a*) properly, a dynamical (time-dependent) formalism of the screening and relaxation of the core-hole is required.¶ However, since screening times are of the order of the inverse of the plasma frequency ($\hbar\omega_p$ about 10 ev for metals), and on the basis of the width of the observed oscillations in the EXAFS spectra, the assumption of a static screened hole is made [as noted previously (13), this is perhaps the most serious approximation of the theory]. Scattering from neighboring ion-cores is described via potential scattering phase-shifts (derived by integration of the radial Schrodinger equation with a muffin-tin potential), and the attenuation of the electron's motion, due to inelastic scattering, is described via the use of a complex optical potential. Finally, the effect of thermal vibrations is included through a Debye-Waller factor. Using a multiple-scattering T matrix propagator formalism in a spherical representation, an expression for the final state wave function, $|f\rangle$, which includes multiple-scattering paths to high-order, is derived‖. The oscillatory component of the photoabsorption cross section originates from the coupling of that part of the electron wave which upon scattering by the medium is turned back towards the central ionized atom, where it couples to the initial state via the dipole operator (Eq. **1b**). This coupling leads to an interference phenomenon, since the scattered photoelectron suffers a shift in phase in reference to the initial outgoing wave—hence the dependence on the microscopic structure of the environment.

We turn now to a brief discussion of the new aspects that are introduced into the theory by the surface. While a more refined multiple-scattering calculation is presented by us elsewhere, it is sufficient for our purpose to consider here a simplified version of the theory. By using the single-scattering and small atom approximation (i.e., neglecting the curvature of the incident wave front) for $kR_j \gg 1$, where R_j is the distance from the central excited atom to the jth shell of neighbors and k is the photoelectrons wave vector $[k = \hbar^{-1} [2m(\hbar(\omega - \omega_T) + V_0)]^{1/2}$, where $\hbar\omega_T$ is the absorption edge energy and V_0 is the inner potential of the solid associated with exchange and correlation, the following expression for the oscillatory component of the photoabsorption cross section (for K-shell excitation) is obtained:

$$\chi(k) = k^{-1}|f(k,\pi)|\sum_j W_j \sin[2kR_j + \alpha(k)] \times \exp(-\gamma R_j - 2\sigma_j^2 k^2), \quad [2]$$

where the atomic scattering factor in a partial-wave expansion with partial wave phase-shifts δ_l is given by (17)

$$f(k,\theta) = (1/k)\sum_{l=0}^{\infty} (2l + 1)[\exp(2i\delta_l(k)) - 1]P_l(\cos\theta). \quad [3]$$

$P_l(x)$ is the lth Legendre polynomial, γ is an attenuation coefficient, $\exp(-2\sigma_j^2 k^2)$ is a Debye-Waller factor, and the weight W_j is given in terms of the number of atoms in the jth shell and their distance as

$$W_j = N_j/R_j^2, \quad [4]$$

and $\alpha(k) = \text{Arg}\,[f(k,\pi)] + 2\eta$, where η is the shift in phase due to the central atom. The above expression (Eq. **2**) formed the basis of a direct, Fourier transform, method of analysis which has been successfully applied to the analysis of EXAFS data (7–10).**

To estimate the contribution of atoms at the surface region to the oscillatory component of the EXAFS signal, we consider a crystalline material of the F.C.C. lattice type which for simplicity is assumed to retain its bulk structure up to the surface plane (modifications can easily be accounted for), and in addition we assume that all other factors in Eq. **2** remain constant (again, allowance for differences between the vibronic characteristics of surface and bulk atoms can be easily included). Under these assumptions the surface contribution can be estimated by calculating the alterations in the number of neighbors of atoms in the topmost layer of the solid. In Table 1 the number of neighbors in the different "coordination shells" are listed $[N_j^{(l)}]$ for atoms in layer 1 to 5 [for the (100) face], along with their fraction of the bulk values $[X_j^{(l)} = N_j^{(l)}/N_j^B]$ and their corresponding weights $(W_j^{(l)})$. Examination of the data in Table 1 reveals that the backscattering contribution from first shell neighbors is ⅔ of the bulk value for atoms in the topmost layer. Thus, only ⅓ of the outgoing wave from top layer ionized atoms would not encounter backscattering events and would not contribute to the oscillatory EXAFS signal, while the other ⅔ of the wave front would contribute (clearly, in normalizing the

¶ As will be discussed below, nonradiative core-hole decay mechanisms occur on the time scale of the photoelectron backscattering roundtrip. The effect of these processes can be accounted for in a proper calculation of η (see Eq. **2** and the expression for α following Eq. **4**).

‖ For details see refs. 12 and 13. An explicit approximate expression (single-scattering) is given in ref. 8.

** A direct method, in the same spirit as the Fourier-EXAFS-transform, for the determination of surface structures from LEED intensities has been independently proposed by the present authors (18–21).

Table 1. Atomic coordination shells and weights for the bulk and (100) surface of an F.C.C. crystal

Shell	Bulk		Layer 1			Layer 2			Layer 3			Layer 4			Layer 5		
no.	N_j^B	W_j^B	$N_j^{(1)}$	$X_j^{(1)}$	$W_j^{(1)}$	$N_j^{(2)}$	$X_j^{(2)}$	$W_j^{(2)}$	$N_j^{(3)}$	$X_j^{(3)}$	$W_j^{(3)}$	$N_j^{(4)}$	$X_j^{(4)}$	$W_j^{(4)}$	$N_j^{(5)}$	$X_j^{(5)}$	$W_j^{(5)}$
1	12	24	8	2/3	16	12	1	24	12	1	24	12	1	24	12	1	24
2	6	6	5	5/6	5	5	5/6	5	6	1	6	6	1	6	6	1	6
3	24	16	12	1/2	8	20	5/6	13.33	24	1	16	24	1	16	24	1	16
4	12	6	8	2/3	4	6	1/2	3	12	1	6	12	1	6	12	1	6
5	24	9.6	16	2/3	6.4	20	5/6	8	20	5/6	8	24	1	9.6	24	1	9.6
6	8	2.7	4	1/2	1.35	4	1/2	1.35	8	1	2.7	8	1	2.7	8	1	2.7
7	48	13.7	24	1/2	6.85	32	2/3	9.133	40	5/6	11.4166	48	1	13.7	48	1	13.7
8	6	1.5	5	5/6	1.25	5	5/6	1.25	5	5/6	1.25	5	5/6	1.25	6	1	1.5

The number of neighbors in the first eight coordination shells and corresponding weights for bulk and surface atoms for an F.C.C. lattice (100 face). The weight W_j (see Eqs. 2 and 4) is equal to N_j/R_j^2 in units of the lattice constant squared, a_α^2 (for example, a_{Cu} = 3.64 Å). N_j^B and W_j^B are the bulk number of neighbors and weights for shell j (j = 1–8), respectively. $N_j^{(l)}$, $X_j^{(l)} = N_j^{(l)}/N_j^B$, and $W_j^{(l)}$ are the number of neighbors in shell j, fraction with respect to the bulk number, and weights, respectively, for atoms in layer l(l = 1–5), with l = 1 taken as the topmost layer.

data, to be described below, appropriate account of these weights should be exercised.)

EXAFS–Auger

The introduction of a core-hole, whose probability of creation is related to the microscopic structure of the environment, as discussed above, triggers various decay mechanisms. These can be of radiative (fluorescence) or nonradiative (Auger and Coster-Kronig transitions) nature. The intensity ratio between the Auger electron and x-ray emissions depends on the atomic number Z. The Auger transition rate results from the electrostatic forces produced by a vacancy in the atomic electronic structure [$T(a \rightarrow b) \propto |\langle b|1/r_{ij}|a\rangle|^2 \rho_F$, where ρ_F is the density of final state and a and b are the orbitals between which the transition occurs]. The rate of x-ray emission is determined by the electromagnetic dipole strength. The probability of photon emissions is given by (22)

$$\kappa = (1 + aZ^{-4})^{-1} \qquad [5]$$

where $a = 1.12 \times 10^6$ for K electrons and 6.4×10^7 for L_{111} electrons and Z is the atomic number. It is thus seen that, for those elements for which K-shell and L-shell ionization is available, photon emission can be neglected (only for elements with $Z > 55$, the radiative decay is a significant competitor). The relation between the lifetime Δt (in sec) and energy spread ΔE (in ev) is given as $\Delta t \cong 6.5 \times 10^{-16}/\Delta E$. Auger decay contributes, usually, about 0.01–0.2 ev to a core-electron width and much more to a valence-electron width (23, 24). (For a review of Auger electron spectroscopy, see ref. 24.)

The largest life-times are for the outermost core levels in the light elements up to potassium. For the transition metals the Auger widths are substantially larger than for the light elements (estimated outermost core level widths for Na, Mg, Al, and K are $10^{-2} - 2 \times 10^{-2}$ ev, and 2×10^{-1} for Ni). From the above, the transition time in Auger emission is of the order of 10^{-14}–10^{-16} sec, depending on the core excitation and the characteristic Auger line considered. This time is of the same order of magnitude as the average time for a photoelectron in the energy range of interest (50–500 ev) to complete a typical "round trip" starting at the ionized center. Consequently, the phase information contained in the photoabsorption cross section can be detected by the Auger process. Hence, for a proper choice of the absorption edge and characteristic Auger transition, measurement of the variation of the intensity in a particular Auger line as a function of incident photon energy would provide a measure of the photoabsorption cross section. In particular, the Auger intensity would contain an oscillatory component from which structural information may be extracted. The surface sensitivity of the process derives from the short escape depth of electrons in the energy range of interest [for energies of 10–10^3 ev the mean escape depth is less than 10 Å (25, 26)].

The number of electrons arriving at the detector with an energy of the characteristic $W_\alpha XY$ Auger line (where W_α is the absorption edge core-level of element α, to which the incident x-ray line has been tuned) can be written as

$$N_{W_\alpha XY}(\hbar\omega) = N_{W_\alpha XY}(\hbar\omega) + N_B(\hbar\omega), \qquad [6]$$

where $N_B(\hbar\omega)$ is a background term to be discussed below and $N_{W_\alpha XY}$ is given by††

$$N_{W_\alpha XY}(\hbar\omega) = (4\pi)^{-1}\zeta_{W_\alpha XY}[1 - \kappa]\int_\Omega\int_0^\infty \rho_\alpha(z)P_{W_\alpha}(\hbar\omega; z) \times \exp[-z/\lambda(W_\alpha XY) \cos\theta]dz d\Omega, \qquad [7]$$

where $\zeta_{W_\alpha XY}$ is the probability that an excited atom will decay via $W_\alpha XY$ Auger transition, $\rho_\alpha(z)$ is the atomic concentration of element α at depth z (assuming homogeneous concentration in the planes), $\lambda(W_\alpha XY)$ is the mean free path for an $W_\alpha XY$ Auger electron, θ is the angle that the escaping Auger electron makes with the surface normal, and κ is the photon emission probability given by Eq. 5 for K and L core-holes (κ can be neglected in most cases). Hence, it is seen that the only factor in Eq. 7 that depends on the energy of the incident photon ($\hbar\omega$) is the photoabsorption probability $P_{W_\alpha}(\hbar\omega)$ and, in turn, oscillation in it as a function of energy would give rise to oscillations in $N_{W_\alpha XY}(\hbar\omega)$. For a crystalline material with uniform layer spacing d, the oscillatory component of Eq. 7 can be written as

$$\chi^A_{W_\alpha XY}(k) = \zeta_{W_\alpha XY}[1 - \kappa]\sum_{j=1}^\infty t_j(k)\sum_{l=1}^\infty W_j^{(l)}\rho_\alpha^{(l)}g^{(l)}, \qquad [8a]$$

$$t_j(k) = k^{-1}|f(k,\pi)| \sin[2kR_j + \alpha(k)] \exp(-\gamma R_j - 2\sigma_j^2k^2), \qquad [8b]$$

$$g^{(l)} = (4\pi)^{-1}\int_\Omega \exp[-(l - 1)d/\lambda \cos\theta]d\Omega, \qquad [8c]‡‡$$

†† With some modification, this equation is similar to that given in ref. 26.

‡‡ Assuming that all the electrons emitted into the upper hemisphere are collected, and since the escape depth is small compared to the sample's dimensions, the integration in Eq. 8c can be performed yielding $g^{(l)} = (2\pi)^{-1} E_2[(l - 1)d/\lambda]$, where $E_2(x)$ is the exponential integral of order 2 (see ref. 27). The function $E_2(x)$ is monotonously decreasing for increasing values of x, with $E_2(0) = 1$.

where j and l are the coordination shell and layer index, respectively, ($l = 1$ being the topmost layer) and all the other terms are as defined in the section, **EXAFS.**

Since in the proposed experiment the intensity of a particular fixed Auger line is measured, all factors but the oscillatory part (varying with energy) are constant for all data points.

The background term, N_B, in Eq. **6** is expected to contain contributions mainly from (*a*) photoelectrons that have lost energy via plasmon (both bulk and surface) excitations, (*b*) secondary electron emission by photoelectrons, and (*c*) secondary Auger processes initiated by the photoelectron. The last contribution can be eliminated by limiting the incident photon energy to less than twice the absorption-edge energy used in the measurement. The second contribution to the background is smoothly varying and could be separated from the oscillatory component. The contribution from (*a*) is perhaps the most troublesome. However, it could be reduced by modulating the incident radiation (either on-line or numerically) and recording the dc component of the signal, or via a subtraction of a calculated multiple-plasmon-yield curve (28)[§§]. In conventional EXAFS measurements, the absorption of x-rays passing through the sample is measured, and the oscillatory component is superimposed on a large background component originating from absorption processes other than the particular core excitation under study. A method for processing the data using background subtraction via the Victoreen formula and a Fourier filtering technique has been developed (9, 10). In the presently proposed experiment, the contribution from such processes is expected to be smaller than in the normal EXAFS measurement, since the measurement is limited to the intensity of electrons emitted at a particular (fixed) energy. In any case, methods similar to those described in refs. 9 and 10 could be used. Finally, we should note that in choosing the Auger line at which the intensity measurements are to be made, one might have to consider shifts of the characteristic Auger energies due to extra-relaxation processes, but these are not expected to depend strongly on the energy of the incident radiation in the range of interest.

EPILOGUE

The microscopic structure of the surface region of solids is fundamental to further understanding of surface phenomena. As part of a continuing intensive effort in the development of spectroscopic techniques for surface structure analysis, we outlined in this note a proposal for a surface sensitive probe, based on a coupling of the extended x-ray absorption edge process and Auger electron emission. Our theoretical considerations indicate that a measurement of the intensity of characteristic Auger lines as a function of the energy of incident radiation would have an oscillatory component that contains structural information. Clearly, an experiment such as proposed in this note requires an ultra-high vacuum environment to assure a well-characterized, reproducible surface condition. In addition it is necessary to use a high flux radiation source, to increase the signal-to-noise ratio, and to enable measurements over short periods of time, which is of importance from both the surface condition and practical aspects. The method is not limited to systems exhibiting long-range order (which is the requirement of most diffraction techniques), and enables one to tune to the environment of specific chemical constituents by choosing the absorption edge to be used. An obvious experiment would be one in which an overlayer (monolayer or less) is deposited on a substrate, and the results of experiments in which the absorption edges of the overlayer atoms and of the substrate are compared. The method has the potentiality of analyzing complex surface structures that are not accessible to other techniques. While it is felt that our theoretical studies provide supporting evidence as to the feasibility and potential of the EXAFS–Auger technique, it is also appreciated that there is no substitute for the experience and information to be derived from the actual experiment. In this sense this epilogue may be regarded not as the end but also as a beginning.

[§§] **Note Added in Proof.** We are grateful to Prof. T. A. Callcott for suggesting to us that the contribution from (*a*) could be eliminated by in-phase modulation of both the photon energy and the sample potential. With such modulation, electrons correlated in energy with the photo-electrons are always detected, but the electron energy analyzer is shifted on and off the Auger peak. By square wave modulation and pulse counting, the "off peak" counts may be subtracted electronically from the "on peak" counts to leave the Auger signal plus the smooth background of secondary electrons.

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1. Hosemann, R. H. & Bagchi, S. N. (1962) *Direct Analysis of Diffraction by Matter* (North-Holland, Amsterdam).
2. Hoppe, W. & Mason, R., eds. (1974) *Advances in Structure Research by Diffraction Methods* (Pergamon, Oxford), Vol. 5.
3. Kossel, W. (1920) *Z. Physik* **1**, 119.
4. Kossel, W. (1920) *Z. Physik*. **2**, 470.
5. Azároff, L. V. (1963) *Rev. Mod. Phys.* **35**, 1012–1022.
6. Van Nordstrand, R. A. (1967) in *Handbook of X-Rays*, ed. Kaelble, E. F. (McGraw-Hill, San Francisco), Chap. 43.
7. Sayers, D. E., Stern, E. A. & Lytle, F. W. (1971) *Phys. Rev. Lett.* **27**, 1204–1207.
8. Stern, E. A. (1974) *Phys. Rev.* **B10**, 3027–3037 and references therein.
9. Lytle, F. W., Sayers, D. E. & Stern, E. A. (1975) *Phys. Rev.* **11**, 4825–4835.
10. Stern, E. A., Sayers, D. E. & Lytle, F. W. (1975) *Phys. Rev.* **11**, 4836–4846.
11. Kincaid, B. M. & Eisenberger, P. (1975) *Phys. Rev. Lett.* **34**, 1361–1364.
12. Ashley, C. A. & Doniach, S. (1975) *Phys. Rev.* **B11**, 1279–1288.
13. Lee, P. & Pendry, J. B., (1975) *Phys. Rev.* **B11**, 2795–2811.
14. Hagstrum, H. D. & McRae, E. G. (1975) in "Adsorption of gases on solids," in *Treatise on Solid State Chemistry*, ed. Hannay, N. B. (Plenum, New York), Vol. 6, in press.
15. Davisson, C. J. & Germer, L. H. (1927) *Phys. Rev.* **30**, 705–740.
16. Rhodin, T. N. & Tong, S. Y. (1975) *Phys. Today*, October, 23–32.
17. Schiff, L. I. (1955) *Quantum Mechanics* (McGraw-Hill, New York).
18. Landman, U. & Adams, D. L. (1974) *J. Vac. Sci. Technol.* **11**, 195–200.
19. Adams, D. L. & Landman, U. (1974) *Phys. Rev. Lett.* **33**, 585–589.
20. Landman, U. & Adams, D. L. (1975) *Surface Sci.* **51**, 149–173.
21. Landman, U. (1975) *Faraday Discussions* **60**, 230–238.
22. Burhop, E. S. H. (1952) *The Auger Effect and Other Radiationless Transitions* (University Press, Cambridge).
23. Hedin, L. (1974) in *X-Ray Spectroscopy*, ed. Azaroff, L. V. (McGraw-Hill, New York), Chap. 5, and references therein.
24. Chang, C. C. (1971) *Surface Sci.* **25**, 53–79.
25. Riviere, J. C. (1973) *Contemporary Phys.* **14**, 513–539.
26. Palmberg, P. W. (1976) *J. Vac. Sci. Technol.* **13**, 214–220.
27. Abramowitz, M. & Stegun, I. A. (1965) *Handbook of Mathematical Functions* (Dover Press, New York), p. 228.
28. Pardee, W. J., Mahan, G. D., Eastman, D. E., Pollak, R. A., Ley, L., McFeely, F. R., Kowalczky, S. P. & Shirley, D. A. (1975) *Phys. Rev.* **B11**, 3614–3616, and references therein.