Abstract: EXAFS-Auger process for surface-structure analysis

Uzi Landman

Institute for Fundamental Studies, Department of Physics and Astronomy, University of Rochester, Rochester, New York 14627

David L. Adams

Institute of Physics, Aarhus University, 8000 Aarhus C, Denmark

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We present theoretical considerations of a proposed novel surface-sensitive probe, based on a coupling of the extended x-ray absorption edge process and Auger electron emission.[1]

In the current theoretical model[2–6] 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.[2] 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 feasiability of extracting geometrical information from the EXAFS signal has been demonstrated via the use of direct, Fourier transform,[2–4] and indirect, model calculation,[5,6] methods of analysis.

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. Several modifications of the original EXAFS experiment can be considered. (i) Measurement of the photoelectron intensity as a function of the incident photon energy: This experiment, while being feasible, does not provide structural information directly proportional to that obtained via the EXAFS process because of the half-space geometry of the electron-detection system. (ii) Measurement of the fluorescence yield due to the photo-ionization process in adsorption systems: The main problem here is the poor signal-to-noise ratio which limits the applicability and resolution of the method. This leads us to the third possibility, which is to monitor the photoabsorption cross section [Fig. 1(a)] by measuring the intensity variation of a particular Auger line [Fig. 1(b)] as a function of the incident photon energy. The surface sensitivity of the total process derives from the short escape length of selected Auger electrons.

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. For elements for which K-shell ionization is available, photon emission can be neglected for elements with $Z < 55$.[7] In addition, from the width of typical Auger lines, it can be estimated that the transition times in the Auger process (10^{-14}–10^{-16} s) 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 "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 could provide a measure of the photoabsorption cross section. In

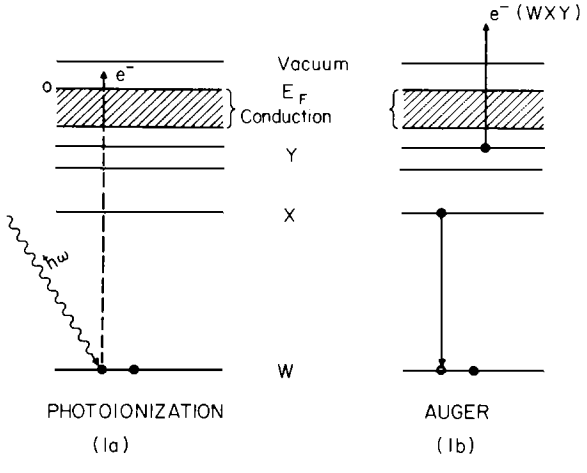


FIG. 1. Schematic description of the EXAFS-Auger process. Electronic energy levels (in a metal) are labeled by W, X, Y, the conduction band is dashed, and the Fermi level is denoted by E_F. (a) The photoionization process—a photon of energy $\hbar\omega$ excites an electron (filled circle, dashed line) 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 which depends on levels W, X, and Y.

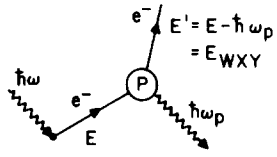
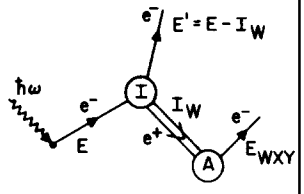
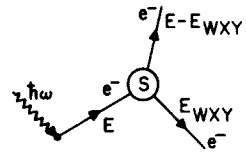
BACKGROUND SOURCE	PROCESS	CURE
PHOTOELECTRONS THAT HAVE EXCITED (BULK AND SURFACE) PLASMONS		IN-PHASE MODULATION OF BOTH THE INCIDENT PHOTON ENERGY AND THE SAMPLE POTENTIAL
SECONDARY AUGER PROCESSES		LIMIT ħω TO LESS THAN TWICE THE ABSORPTION-EDGE ENERGY USED IN THE MEASUREMENT (ħω < 2I_W)
SECONDARY ELECTRON EMISSION		SMOOTHLY VARYING - SUBTRACTION

FIG. 2. Sources of background contributions, schematic descriptions of the processes, and suggested "cures." The vertices denoted by P, I, A and S designate plasmon creation, electron-impact ionization, Auger process, and secondary-electron creation, respectively. A wavy line denotes the incident photon propagation, a solid line, electron propagation, and a double line, a hole propagator.

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).

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[1]

$$N^t_{W\alpha XY}(\hbar\omega) = N_{W\alpha XY}(\hbar\omega) + N_B(\hbar\omega), \qquad (1)$$

where $N_{W_\alpha XY}(\hbar\omega)$ contains an oscillatory (structure related) component and $N_B(\hbar\omega)$ is a background term.[1] The main contributions to the background and schematic descriptions of the processes are summarized in Fig. 2. In addition, suggested "cures" are included. 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.[4] 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 earlier described[4] could be employed.[8] It should also be emphasized that to ensure reproducible, well-characterized surface conditions, a UHV environment is necessary. In order to maintain clean surface conditions for the extent of the measurements, a high-flux radiation source (synchotron radiation from a storage ring[9]) should be used. The use of such a source has also a decisive advantage over conventional sources in terms of the sinal-to-noise ratio and the practical aspects of the technique.

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