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PHOTOEMISSION BY POLARIZED X-RAYS

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The angular distribution of photoelectrons excited by X-rays is strongly correlated with the degree and type of polarization of incident photons. The angular and energy spectrum of signal photoelectrons leaving a solid is considerably modified as compared to the differential photoelectric cross-section owing to elastic and inelastic collisions the electrons suffer on their way out of a target. In this report an analytical expression for the angular distribution of photoelectrons escaping from the sample without being scattered inelastically was found in the transport approximation. The dependence of the angular distribution on the parameters characterizing optical orientation and polarization of incident X-rays was studied in detail.

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1. Introduction

A huge gain in brightness of the third generation of synchrotron radiation sources has opened new areas of X-ray photoelectron spectroscopy (XPS) applications to surface analysis. In particular, X-ray photoemission spectromicroscopy [1] and X-ray standing wave induced photoemission [2] have been developed as effective tools for surface studies. In addition to traditional advantages such as non-destructiveness and multi-elemental detection capability, synchrotron radiation based XPS offers unique opportunities for continuous variation of photon energy and a possibility of focusing a photon beam into a small spot [3]. Another important feature of synchrotron radiation is a high degree of polarization in the electron orbit plane. Generally, circularly polarized radiation is emitted slightly above and below storage ring plates while X-rays propagating in the ring planes are linearly polarized [4].

The initial angular distribution of X-ray excited photoelectrons is strongly correlated with the type and degree of polarization of an incident wave. Signal electrons (i.e. those that do not lose a considerable amount of their initial kinetic energy) escaping from a solid suffer multiple elastic and inelastic collisions. As a result, the angular and energy distribution of the photoelectron line intensity may be considerably modified as compared to the differential photoelectric cross-section. Recently it has been shown that there exists an interesting optical orientation transfer to the escape probability of signal photoelectrons [5]. For instance, their

mean escape depth depends strongly on both polarization of incident photons and XPS geometrical configuration [5]. In this report, the major attention is paid to studying the influence of elastic and inelastic collisions on the angular distribution of the signal photoelectron line intensity.

2. Theory

A photon beam of arbitrary polarization can be most generally described by the density matrix ρ. This matrix can be expanded in the complete basis set of 2×2 matrices i.e. a unit 2×2 matrix and the three Pauli matrices [6]. The expansion coefficients in this representation are proportional to the components of the four-dimensional vector $\{1, S_1, S_2, S_3\}$, where S_i are the Stokes parameters. The Stokes parameters are related to the degree and the type of polarization p and η, respectively, and the azimuthal orientation γ of the polarization vector by the expressions

$$S_1 = p\cos 2\eta \cos(\pi + 2\gamma), \tag{1}$$

$$S_2 = p\cos 2\eta \sin(\pi + 2\gamma), \tag{2}$$

$$S_3 = p\sin 2\eta. \tag{3}$$

Thus, mathematically, the three quantities p, η and $\pi + 2\gamma$ represent spherical coordinates of the vector $\boldsymbol{S} = \{S_1, S_2, S_3\}$ so that $S = p$. To allow for the right and left elliptical polarization the parameter η is chosen to vary between $-\pi/2$ and $\pi/2$. The quantity γ is equal to the angle between the x-axis and the principal axis of the polarization ellipse and is restricted to the range $(0, \pi)$ (here a local coordinate system xyz is chosen with the z-axis directed along the photon propagation direction).

The angular distribution of photoelectrons ejected from an amorphous solid can be found from the expression

$$Y(\Omega) = y_0 \int G(\Omega, \Omega_0) f(\Omega_\gamma, \Omega_0) \mathrm{d}\Omega_0 \qquad (y_0 = n_0 \sigma_{\mathrm{ph}} F), \tag{4}$$

where n_0 is the atomic bulk density, F is the photon flux, σ_{ph} and $f(\Omega_\gamma, \Omega_0)$ are the total and normalized differential photoelectric cross-sections respectively. The unit vectors Ω and Ω_0 describe the photoelectron emission directions from the sample and atoms, correspondingly, while the quantity Ω_γ specifies the photon propagation direction. The quantity $G(\Omega, \Omega_0)$ in the integrand of the right-hand side of Eq. (4) represents a response function. If there were no elastic scattering of electrons the function G would be proportional to $\delta(\Omega - \Omega_0)$ and the angular distribution of the signal intensity would be completely determined by the differential photoelectric cross-section. However, elastic collisions redistribute signal electrons over emission directions and increase effectively path lengths travelled by particles before leaving a solid. Since the probability for an electron to be scattered inelastically augments with increasing travelled path length the elastic interaction tends to diminish the overall photoelectron yield from the target. It should be stressed that Eq. (4) is valid for an arbitrary differential photoelectric cross-section and, therefore, can be used to describe excitation of photoelectrons from different core shells.

An explicit expression for the response function $G(\Omega, \Omega_0)$ can be found by solving a kinetic equation with an appropriate boundary condition in the transport approximation [7]. This approximation meets the requirements imposed by the so-called generalized radiative field similarity principle [8] and allows to simplify the elastic collision integral in the transport equation to obtain an analytical solution of the boundary value problem. The important feature of the transport approximation is that it provides an approximate solution which is quite close to the exact one for any value of the scattering parameter $\chi = \lambda_i/\lambda_{tr}$, where λ_i and λ_{tr} are the inelastic and the transport mean free paths of signal electrons. The analytical results found in this way compare well with those obtained from Monte Carlo simulations based on a realistic Mott differential elastic scattering cross-section [7, 8].

The initial angular distribution of photoelectrons, as a function of the Stokes parameters in the coordinate system XYZ related to the target (this system is obtained from the system xyz by rotation at the angle θ_γ around the y-axis, where θ_γ is the X-ray angle of incidence, counted from the surface normal [5]) has been recently found [5]. Making use of results of Refs. [5] and [7] and performing integration over the initial emission directions in formula (4) we arrive at the final expression for differential photoelectron yield

$$Y(\alpha, \phi) = (y_0 \lambda \cos\alpha/4\pi)\Big\{(1-\omega)^{-1/2} H(\cos\alpha, \omega)$$

$$-(\beta/4)(3\cos^2\Theta - 1 + 3S_1\zeta_1 + 3S_2\zeta_2) + (\omega\beta/16)[3\mu_\gamma^2 - 1 + 3S_1(1-\mu_\gamma^2)]$$

$$\times \int_0^1 x H(x, \omega) H(\cos\alpha, \omega)(3x^2 - 1)(x + \cos\alpha)^{-1} \mathrm{d}x \Big\}. \tag{5}$$

In formula (5) α and ϕ are the polar and azimuthal emission angles counted from the surface normal and the X-ray plane of incidence, respectively; $\mu_\gamma = \cos\theta_\gamma$; β is the asymmetry parameter; $H(x, \omega)$ is the H-function of Chandrasekhar [9]; λ is the total mean free path in the transport approximation,

$$\lambda = \lambda_i \lambda_{tr}/(\lambda_i + \lambda_{tr}) \tag{6}$$

and $\omega = \lambda/\lambda_{tr}$ is the single scattering albedo. The functions $\zeta_i = \zeta_i(\alpha, \phi)$ $(i = 1, 2)$ read

$$\zeta_1(\alpha, \phi) = \cos^2\theta_\gamma \sin^2\alpha \cos 2\phi + \cos\theta_\gamma \sin\theta_\gamma \sin 2\alpha \cos\phi$$

$$+ \sin^2\theta_\gamma(\cos^2\alpha - \sin^2\alpha \cos^2\phi), \tag{7}$$

$$\zeta_2(\alpha, \phi) = \cos\theta_\gamma \sin^2\alpha \sin 2\phi + \sin\theta_\gamma \sin 2\alpha \sin\phi. \tag{8}$$

As it follows from Eq. (5) the influence of elastic and inelastic scattering on the angular distribution is accounted for by means of the transport and the inelastic mean free paths. Note that distribution (5) depends only on the two Stokes parameters, S_1 and S_2. Therefore, the angular distribution of photoelectrons excited by unpolarized X-rays ($p = 0$) is the same as that induced by circularly polarized photons ($p = 1$, $\eta = \pm 45°$).

3. Results and discussion

Analysis of expression (5) shows that elastic scattering makes the angular distribution of a signal line intensity smoother as compared to the differential photoelectric cross-section. Thus, the number of photoelectrons emitted from the sample in the directions of maxima of the photoelectric cross-section is decreased while the relative intensity in the directions pertaining to minima of the initial angular distribution is increased. This effect is illustrated in Figs. 1 and 2. In Fig. 1 the normalized angular distribution $8\pi Y(\Omega)/y_0\lambda\cos\alpha$ of Pt $4s$ photoelectrons ($\beta = 1.80$) ejected from a platinum target by completely polarized ($p = 1$) and unpolarized ($p = 0$) radiations is shown by solid curves. The distributions are displayed versus azimuthal angle for the geometry $\theta_\gamma = \alpha = 45°$. The energy of photons corresponds to Al K_α radiation so that the photoelectron energy is equal to 763 eV. X-rays are assumed to be linearly polarized along y-axis, i.e. parallel to the target surface. It is seen that varying the degree of polarization of X-rays changes drastically the character of the angular distribution. For instance, the maxima of the photoelectron yield for unpolarized radiation are in the plane of photon incidence while in the case of polarized X-rays they are in the plane perpendicular to that of X-ray incidence. The values of the transport and inelastic mean free paths ($\lambda_{tr} = 10.8$ Å and $\lambda_i = 17.2$ Å) were found by direct integration of the differential elastic scattering cross-section [7] and by the formula of Tanuma et al. [10], respectively. The scattering parameter for platinum in the case considered is $\chi = 0.62$ and one may expect pronounced effects of elastic scattering. Also shown by dashed lines are the azimuthal distributions of photoelectrons, calculated in the

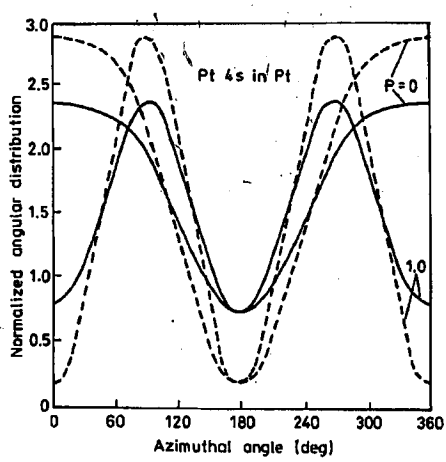

Fig. 1. The normalized angular distribution of Pt $4s$ photoelectrons ejected from a platinum target in the direction $\alpha = 45°$ by unpolarized ($p = 0$) and linearly polarized ($p = 1.0$, $\eta = 90°$) X-rays incident on the target at the angle $\theta_\gamma = 45°$. Solid and dashed curves are the results of calculations from formula (5) with and without accounting for elastic scattering of photoelectrons, respectively.

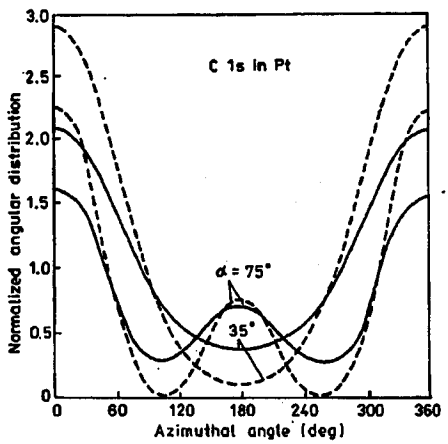

Fig. 2. The normalized angular distribution of C 1*s* photoelectrons escaping from a platinum target without being scattered inelastically in the directions specified by the polar emission angle $\alpha = 35°$ and 75°. X-rays are incident at the angle $\theta_\gamma = 45°$ and are linearly polarized along the x-axis (see text for explanations). Solid curves are the results of calculations from formula (5). Dashed curves are the straight line approximation results (elastic scattering is neglected).

straight line approximation when elastic scattering is neglected. These results are obtained formally by putting $\lambda_{tr} = 0$ in formula (5). One can see that disregard for elastic collisions may lead to under- or overestimating the photoelectron yield by about 20–200% depending on the geometry.

As another example, Fig. 2 displays the azimuthal distributions of C 1*s* photoelectrons ($\beta = 2.0$) escaping from a platinum target in the directions specified by two different polar emission angles: $\alpha = 35°$ and 75°. Signal electrons are excited by a completely polarized ($p = 1$) beam of X-rays incident on the surface at the angle $\theta_\gamma = 45°$. The energy of photoelectrons is chosen to be the same as in Fig. 1. The incident wave is now linearly polarized along the x-axis, i.e. parallel to the plane on incidence ($\eta = 0$, $\gamma = 0$). Solid curves represent the results of calculations by formula (5) multiplied by the factor $4\pi/y_0\lambda\cos\alpha$ to get approximately the same scale as in Fig. 1. From Fig. 2 it follows that for the emission angle $\alpha = 35°$ the azimuthal distribution reaches its minimum value at $\phi = 180°$ since the emission direction (35°, 180°) is almost perpendicular to the direction of the polarization vector in the incident wave (the *s*-photoelectrons are pushed from atoms predominantly in the directions of the electric field vector oscillations). As the polar emission angle increases up to 75° this minimum splits into two off-plane minima located at $\phi = 106°$. In absence of elastic scattering these minima correspond to zero probability for an electron to be emitted from the target (cf. dashed curves in Fig. 2). From Fig. 2 it is seen, however, that accounting for elastic collisions leads to appearance of a noticeable signal intensity in the direction (75°, 106°) prohibited by the dipole selection rules. On the other hand, the intensity of the C 1*s* photoelectron line in the directions of maxima

($\phi = 0,\ 360°$) of the differential photoelectric cross-section is decreased by about 40% due to elastic scattering.

In conclusion, two points are to be emphasized. First, elastic collisions of electrons on their way out of the target influence strongly the angular distribution of a photoelectron current, especially for materials with high atomic numbers. Secondly, the angular dependence of the photoelectron line intensity is correlated with the photoelectric differential cross-section and, therefore, photoemission from solids by polarized X-rays can be used, in principle, to determine the Stokes parameters S_1 and S_2 experimentally. However, an appropriate correction for the elastic scattering effect should be made in the latter case.

Acknowledgments

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