Secondary-electron energy distribution in high-energy photoemission

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(Received 21 September 1976)

We have calculated the energy distribution of secondary electrons observed in core-level XPS or core-level synchrotron photoemission experiments on Al. The secondary electrons are produced when the photoexcited primary electrons scatter inelastically from the valence electrons via the mechanisms of bulk and surface plasmon production and electron–hole production. The scattering cross sections for these events are determined from the Lindhard dielectric function, although the plasmon dispersion and broadening are taken from experimental measurements. Multiple scattering is taken into account by means of the Wolff–Spencer–Fano integral equation for the electron-energy distribution. The calculated results are compared to experiment.

PACS numbers: 79.60.Cn, 79.20.Hx, 71.45.Gm

I. INTRODUCTION

In ESCA (electron spectroscopy for chemical analysis) experiments on solids, high-energy photons (of energy $\hbar\omega$) are used to excite electrons from the core levels of the atoms composing the crystal. Those photoelectrons which escape from the solid are energy analyzed and in general a narrow peak in the electron intensity is observed at an energy $\hbar\omega$ above the core level. This peak is referred to as the elastic line. Also observed are inelastic lines, i.e., broader peaks at lower energies corresponding to photoelectrons that have lost energy by plasmon or electron-hole creation as they traveled to the surface.

In this paper I develop a theory of the inelastic (or secondary) spectrum of photoelectrons observed in ESCA experiments from core levels in nearly free-electron materials. Numerical application is made to the case of ESCA from the $2p$ core level of Al. The theory includes the effects of scattering by bulk and surface-plasmon production, as well as scattering by electron-hole creation. The dispersion and broadening of the plasmons is taken into account. Multiple scattering is included in the theory by the use of a transport equation. Previous workers[1,2] have neglected electron-hole scattering as well as plasmon dispersion and broadening, all of which are important in determining the inelastic energy spectrum.

The calculation is divided into two parts. In Sec. II the energy distribution of the secondaries in the bulk is determined, and in Sec. III the internal bulk distribution is related to the distribution outside the solid, i.e., the observed distribution. The internal and external distributions differ because of inelastic scattering by surface plasmons. In Sec. IV the results of a calculation for the inelastic ESCA distribution from the $2p$ core level in Al is compared to experiment.

A more detailed version of this work will be published in the *Physical Review*.

II. INTERNAL ELECTRON DISTRIBUTION

Following Wolff[3] the equation for the number of electrons with energy E per unit volume, $N(E,\theta,\phi)$, traveling in a direction (θ,ϕ) with respect to the surface normal is

$$\begin{aligned}(v(E)/l(E))N(E,\theta,\phi) \\ + N(E,\theta,\phi)\textstyle\int d\Omega' P(E,\theta',\phi';E,\theta,\phi) \\ = n_0(E,\theta,\phi) + \textstyle\int d\Omega' N(E,\theta',\phi')P(E,\theta',\phi';E,\theta,\phi) \\ + \int_E^\infty dE' \textstyle\int d\Omega' N(E',\theta',\phi')P(E',\theta',\phi';E,\theta,\phi),\end{aligned} \quad (1)$$

where $n_0(E,\theta,\phi)$ is the rate at which electrons are photoexcited into the state (E,θ,ϕ) and $P(E,\theta,\phi;E',\theta',\phi')$ is the probability per unit time that an electron scatters from the state (E,θ,ϕ) to (E',θ',ϕ'). The Auger process in which an electron scatters from (E,θ,ϕ) to say (E'',θ'',ϕ'') while a valence electron is excited to (E',θ',ϕ') can be neglected because E is large (greater than 200 eV.). $v(E)$ is the velocity of an electron with energy E and the electron mean free path for inelastic scattering, $l(E)$, is given by

$$\frac{1}{l(E)} = \frac{1}{v(E)} \int_\mu^E dE' \int d\Omega' P(E,\theta,\phi;E',\theta',\phi'), \quad (2)$$

where μ is the Fermi energy of the solid.

The scattering probability P peaks in the forward direction and consequently Eq. (1) gives

$$\frac{\Phi(E,\theta,\phi)}{l(E)} = n_0(E,\theta,\phi) + \int_E^\infty dE' \Phi(E',\theta,\phi)\tau(E',E) \quad (3a)$$

where

$$\Phi(E,\theta,\phi) = v(E)N(E,\theta,\phi) \quad (3b)$$

and

$$\tau(E',E) = \frac{1}{v(E')} \textstyle\int d\Omega' P(E',\theta',\phi';E,\theta,\phi). \quad (3c)$$

$\Phi(E,\theta,\phi)$ is the flux of electrons traveling in the direction (θ,ϕ) and $\tau(E',E)$ is the probability per unit path length that an electron scatters from the state E to the state E'. It is clear from Eq. (3a) that the assumption of forward scattering has the consequence that elastic scattering determined by $P(E\theta',\phi';E\theta,\phi)$ in Eq. (1) does not affect the electron distribution $\Phi(E,\theta,\phi)$.

The rate at which electrons are photoexcited is given by

$$n_0(E,\theta') = [1 + (\beta/2)(\tfrac{3}{2}\sin^2\theta' - 1)]n_0(E), \tag{4}$$

where θ' is the angle between the incident photons and the path of the photo-excited electron. Over the range of energies of interest to us β can be regarded as independent of E. β is a number of order one and its explicit value depends on whether the excitation takes place from s, p, or d core levels. If the photon beam is at an angle ψ with respect to the normal to the surface then n_0 is given by

$$n_0(E,\theta,\phi) \equiv f(\theta,\phi)n_0(E) \tag{5}$$

$$= \{1 + (\beta/4)(1 - 3[\sin\theta \sin\psi \cos\phi + \cos\theta \cos\psi]^2)\}n_0(E),$$

where (θ,ϕ) are measured with respect to a coordinate system with the z axis normal to the surface and x axis in the plane determined by the surface normal and the direction of the incident photons. Equations (3a) and (5) imply that

$$\Phi(E,\theta,\phi) = \Phi(E)f(\theta,\phi), \tag{6}$$

where f is given by Eq. (5). Equation (3a) then becomes

$$\frac{\Phi(E)}{l(E)} = n_0(E) + \int_E^\infty dE'\Phi(E')\tau(E',E). \tag{7}$$

Equation (7) can be solved numerically given $\tau(E',E)$. It takes proper account of the multiple scattering of the electrons.

The scattering probability per unit path length for a free-electron-like metal is given by[4]

$$\tau(E,E') = (\pi a_0 E)^{-1} \int \frac{d\bar{q}}{\bar{q}} \operatorname{Im}\left(\frac{1}{\epsilon(\bar{q},E-E')}\right), \tag{8a}$$

where a_0 is the Bohr radius, $\bar{q} = q/k_f$ is the momentum transfer q relative to the Fermi momentum k_f, and ϵ is the Lindard dielectric function. The integral in Eq. (8) is carried out over values of $\bar{q}$ that satisfy

$$(\bar{E} - \bar{E}' + \bar{q}^2)/2\bar{q}\sqrt{\bar{E}} < 1. \tag{8b}$$

There are two regions in $\bar{q}$ space which contribute to the integral in (8a): region (a), the region in which Im $\epsilon(q,E-E')$ is nonzero, corresponds to inelastic scattering by creation of electron–hole pairs; and region (b), in which Im $\epsilon(q,E-E') = 0$ and Re $\epsilon(q,E-E') = 0$ so that

$$\operatorname{Im}\left(\frac{1}{\epsilon(q,E-E')}\right) = \frac{\operatorname{Im}(\epsilon)}{[\operatorname{Re}(\epsilon)]^2 + [\operatorname{Im}(\epsilon)]^2} \to -\pi\delta(\operatorname{Re}\epsilon(q,E-E')). \tag{9a}$$

Region (b) corresponds to inelastic scattering due to plasmon creation. In order to include the effects of the broadening of the plasmons on $\tau(E,E')$ we use

$$\operatorname{Im}\left(\frac{1}{\epsilon(q,\omega)}\right) = \frac{{\omega_p}^2\tau_q\omega}{(\omega^2 - {\omega_q}^2)^2 + (\tau_q\omega)^2} \tag{9b}$$

in Eq. (8a) when q lies in region (b). In Eq. (9) ω_p is the plasma frequence of the electron gas, ω_q is the experimentally measured[5] plasmon-dispersion relation, and τ_q is determined from the experimentally measured[5] broadening of the plasmons.

The distribution of electrons in the solid can now be determined from a numerical solution of Eq. (7).

III. EXTERNAL ELECTRON DISTRIBUTION

The distribution of electrons escaping from the solid differs from the internal distribution primarily because of inelastic electron scattering by surface plasmons. The energies of interest to us are sufficiently large that the electron escape probability is unity. The inelastic scattering probability due to the surface can be deduced as follows. The self-energy of an electron with energy E due to the presence of the surface is given approximately by[6]

$$\Sigma(\mathbf{r},\mathbf{r}';E) = (i\hbar/2\pi)\oint d\omega g_0(\mathbf{r},\mathbf{r};E-\omega) \times \int \frac{d^2q_\parallel}{(2\pi)^2}\left(\frac{1-\bar{\epsilon}}{1+\bar{\epsilon}}\right)\frac{2\pi e^2}{q_\parallel} \times \exp[i\bar{\mathbf{q}}_\parallel\cdot(\bar{\mathbf{p}}_\parallel - \bar{\mathbf{p}}_\parallel') - q_\parallel(|z| + |z'|)], \tag{10a}$$

where g_0 is the free-electron Green function, $\mathbf{q}_\parallel$ is a momentum vector parallel to the surface and[7]

$$\bar{\epsilon} = \bar{\epsilon}(q_\parallel,\omega) = \frac{q_\parallel}{\pi}\int_{-\infty}^{\infty}\frac{dq_z}{q^2\epsilon(q,\omega)}. \tag{10b}$$

From Eq. (10) it follows that the imaginary part of the self energy of an electron with momentum $\mathbf{k}$ and energy $\epsilon_k = (\hbar^2/2m)k^2$ is

$$\operatorname{Im}\Sigma_{\mathbf{k},\epsilon_k} = (4e^2/2L\pi^2)\int d\omega \int d^3q(q_\parallel/q^4) \operatorname{Im}[1 + \bar{\epsilon}(\mathbf{q}_\parallel,\omega)]^{-1} \times \delta(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}-\mathbf{q}} - \hbar\omega) \tag{11}$$

The average number of plasmons created when an electron travels from inside the solid through the surface is

$$Q_{\mathbf{k},\epsilon_k} = L/v_z\langle t\rangle, \tag{12a}$$

where L is the distance traveled by the electron, v_z is its velocity normal to the surface and $\langle t\rangle$ is the average time between scattering events

$$1/\langle t\rangle = (2/\hbar)\operatorname{Im}\Sigma_{\mathbf{k},\epsilon_k}. \tag{12b}$$

Use of Eq. (11) in Eq. (12) yields

$$Q_{\mathbf{k},\epsilon_k} \equiv Q(\epsilon_k;\theta,\phi) = \int d\bar{\omega}Q(\epsilon_k,\bar{\omega},\theta,\phi), \tag{13a}$$

where $\mathbf{k}$ is at an angle (θ,ϕ) to the surface normal and

$$Q(E,\bar{\omega},\theta,\phi) = \frac{2}{\pi^2 a_0 k_f \bar{E}}\int_{\bar{\omega} < 2\bar{q}\bar{E} - \bar{q}^2}\frac{d\bar{q}}{\bar{q}^2}\int_0^{2\pi}d\phi \times [1 - (\sin\theta\sin\delta\cos\phi + \cos\theta\cos\delta)^2]^{1/2}\operatorname{Im}[1 + \bar{\epsilon}]^{-1}, \tag{13b}$$

where $\delta = \delta(\bar{q},\bar{\omega})$ is given by

$$\cos\delta = (\bar{\omega} + \bar{q}^2)/2\bar{q}\sqrt{\bar{E}}. \tag{13c}$$

$Q(E,\bar{\omega},\theta,\phi)$ is the average number of collisions made by an electron of energy E moving in a direction (θ,ϕ) going from inside the metal to outside in which it loses energy $\bar{\omega} = \omega/\mu$. Because the surface plasmon scattering takes place very near the surface the quantity, Q is independent of where in the solid the photoelectron was excited. In the limit of very high energies and $\theta = 0$. Eq. (13a) gives $Q = (e^2/\hbar v)(\pi/2)$ in agreement with Ritchie.[8]

The relationship between the distribution of electrons outside the metal to that inside the metal (and determined in Sec. II) is

$$N_{\text{out}}(E,\theta,\phi) = N_{\text{in}}(E,\theta,\phi)[1 - P_T(E,\theta,\phi)] - \int_E^{\infty} \int d\Omega' N_{\text{in}}(E'\theta'\phi')P(E',\theta',\phi';E,\theta,\phi) \quad (14)$$

where $P_T(E,\theta,\phi)$ is the probability that an electron is scattered out of the state (E,θ,ϕ) by surface plasmons and $P(E',\theta',\phi';E,\theta,\phi)$ is the probability that an electron is scattered from (E',θ',ϕ') to (E,θ,ϕ). P_T is related to P by the equation

$$P_T(E,\theta,\phi) = \int_{\mu}^{E} dE' \int d\Omega' P(E,\theta,\phi;E',\theta',\phi'). \quad (15)$$

For high energies the scattering is primarily forward and Eq. (14) becomes

$$\Phi_{\text{out}}(E,\theta,\phi) = \Phi_{\text{in}}(E,\theta,\phi)[1 - P_T(E,\theta,\phi)] + \int_E^{\infty} dE' v(E')^{-1}\Phi_{\text{in}}(E',\theta,\phi)P(E',E;\theta,\phi), \quad (16)$$

where $P(E',E,\theta,\phi)$ is the probability that an electron in the state (E',θ,ϕ) is scattered to a state of energy E. For high energies and $\theta \lesssim \pi/4$ one finds $P,P_T \ll 1$ and consequently

$$P(E',E;\theta,\phi) \simeq Q(E',E' - E,\theta,\phi) \quad (17a)$$

$$P_T(E,\theta,\phi) \simeq Q(E,\theta,\phi), \quad (17b)$$

where Q is given by Eq. (13).

From Eqs. (16) and (13) we see that the distribution of flux outside the metal is determined from that inside the metal once $\bar{\epsilon}$, as specified by Eq. (10b), is known. We assume that

$$\text{Im}[1 + \bar{\epsilon}_q(q_{\|},\omega)]^{-1} = \tfrac{1}{2}\omega_s^2 \omega \tau_{q_{\|}} / [(\omega^2 - \omega_{q_{\|}}^2)^2 + (\omega \tau_{q_{\|}})^2], \quad (18)$$

where ω_s is the surface plasmon frequency at $q = 0$ and ω_q and $\tau_{q_{\|}}$ are determined by the experimentally measured values of the surface plasmon dispersion and broadening.

The theory of Secs. II and III predicts the inelastic loss spectrum given the direction of incident photons, the collection angles or angles of the detector, and the shape of the elastic line, i.e. the source function.

IV. NUMERICAL RESULTS

I now use the theory of Secs. II and III to calculate the inelastic loss observed in ESCA from the $2p$ core level of Al. The data was supplied by Reed McFeely.[10] We only consider energies within about 35 eV of the elastic peak because the $2s$ elastic peak appears 45 eV below the $2p$ peak and interferes with the $2p$ spectrum.

The input needed from experiment is (a) the observed elastic peak, (b) the angle of the detector with respect to the surface normal, which determines the strength of the electron–surface-plasmon coupling, (c) the bulk plasmon dispersion and broadening, and (d) the surface plasmon dispersion and broadening. The observed peak is of course obtained from McFeely's data. For convenience I have fitted the observed peak to a Lorentzian of the same half-width and height. This results in an over estimate in the area under the peak of about 10%–15%. The angle of the detector with respect to the surface normal was about 52°. The bulk-plasmon dispersion is adequately predicted by the Lindhard dielectric function. I have used $r_s = 2.14$, the value for which the plasmon energy is 15.0 eV. The plasmon broadening at $q = 0$ is obtained from optical experiments to be 1 eV, full width at half maximum. The dependence of the broadening on wave number q is obtained from electron-transmission experiments.[11,12] The surface plasmon broadening and dispersion are obtained from inelastic LEED.[13,14] The $q = 0$ values are 10.3 eV for the surface plasmon energy and 1.5 eV. for the broadening.

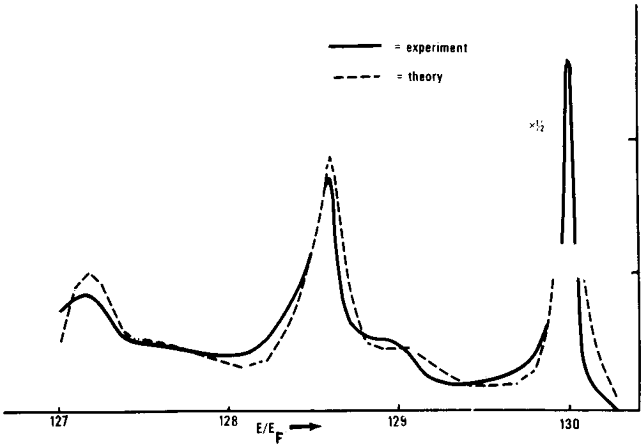

FIG. 1. The solid line represents the experimental data of McFeeley for the $2p$ ESCA spectrum from Al. Intensity in arbitrary units is plotted versus energy in units of $\epsilon_f = 10.85$ eV. The dashed curve represents the results of the theory.

The results of the calculation are shown in Fig. 1. The agreement between theory and experiment is very good and seems to rule out any substantial contribution from intrinsic plasmons (which were not included in the calculation).

ACKNOWLEDGMENTS

We are very grateful to Dr. McFeely for sending us his data and to C. Powell for a number of useful discussions.

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