Theory of the Electron Energy-Loss Spectrum in Core-Level X-Ray Photoemission from Solids

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I present a theory of the electron energy-loss spectra observed in x-ray photoemission from the core levels of solids and report on calculations for the 2*s* and 2*p* core levels of Al, Mg, and Na. The calculation takes intrinsic as well as extrinsic plasmons into account, and in all cases the agreement between theory and experiment is very good.

This Letter is concerned with the electron energy-loss spectra observed in x-ray photoemission spectroscopy (XPS) from core levels of solids. I present a theory of the XPS loss spectra and report the first quantitative calculations of such spectra. The calculations are carried out for photoemission from the 2*s* and 2*p* core levels of Al, Mg, and Na as well as for the Na 1*s* level. In all cases the agreement between theory and experiment is very good. A detailed understanding of the electron energy-loss mechanisms in solids is essential to answering the old question of whether a particular spectroscopy measures a bulk or surface property. It is also a prerequisite for quantitative surface analysis by photoemission or Auger spectroscopy.

The main features of a typical loss spectrum of a free-electron–like metal are several peaks centred at energies E_0, $E_0-\hbar\omega_p$, $E_0-2\hbar\omega_p$ etc., where $\hbar\omega_p$ is the plasmon energy. The peaks represent electrons that have excited zero, one, two, etc., plasmons prior to escaping from the solid. Lundqvist[1] has suggested that an intrinsic process may also be important, namely one in which the core electron is photoexcited and simultaneously one or more plasmons are created by the sudden appearance of the core hole potential. This process results in photoexcited electrons at energies centered at $E_0-\hbar\omega_p$, $E_0-2\hbar\omega_p$, etc., and it is important to know what portion of the loss spectrum is due to these intrinsic processes. Lundqvist[1] suggested over 50% while a more recent semiphenomenological analysis by Pardee *et al.*[2] indicated 10% or less for Al, Mg, and Na. The question has generated much controversy and has yet to be decided by direct experiment. I find the fraction of the first loss peak (the loss spectrum between $E_0-\frac{1}{2}\hbar\omega_p$ and $E_0-\frac{3}{2}\hbar\omega_p$) due to intrinsic processes to lie between the estimates of Lundqvist[1] and Pardee *et al.*[2]

Lucas, Šunjić, and Šokčevic[3] have used a model Hamiltonian that allows an exact solution to study the loss spectra in solids and thin films. However, the Hamiltonian takes only electron-plasmon scattering into account and admits of a simple solution only if the plasmons are dispersionless. I adopt a different approach based on a three-step model[4]: (a) photoexcitation of electrons, (b) transport to the surface, and (c) escape through the surface.

(a) *Electron photoexcitation*: Photoexcitation produces not only electrons centred at E_0 but at $E_0-\hbar\omega_p$, $E_0-2\hbar\omega_p$, etc., as well due to intrinsic plasmon production. The entire group of electrons constitutes the source distribution $s(E)$ which satisfies[5,6]

$$s(E)=(E_0-E)^{-1}\int_E^\infty dE's(E')\alpha(E'-E), \qquad (1a)$$

where

$$\alpha(\omega)=-\frac{1}{\pi}\sum_q\frac{V_q^2}{v_q}\frac{1}{\omega}\mathrm{Im}\left[\frac{1}{\epsilon(q,\omega)}\right], \qquad (1b)$$

and $\epsilon(q,\omega)$ is the momentum- and energy-dependent dielectric function of the solid, V_q is the core hole potential, and $v_q=4\pi e^2/q^2$. Equation (1) is valid for $E_0-E\gg\hbar\gamma_0$, where $\hbar\gamma_0$ is the width of the experimental no-loss line centered at E_0. $s(E)$ is obtained for all energies by taking it to be the experimentally observed no-loss line for $E>E_0-E_c$, where $E_c\approx\frac{1}{2}\hbar\omega_0$ and solving Eq. (1a) for $s(E)$ at energies $E<E_0-E_c$.

It is implicit in Eq. (1) that the photoexcited electron does not interfere with the core hole potential; however, recent work by Chang and Langreth[7] suggests such an interference effect is important and can be viewed as a reduction of the intrinsic plasmon production determined by Eq. (1). The predicted reduction based on a model which neglects electron-hole excitations and plasmon dispersion and broadening is roughly[8] 50%, 35%, and 20% for the 2*s* and 2*p* core levels of Al, Mg, and Na, respectively, and 40% for the Na 1*s* level. Nevertheless, I obtain very good agreement between theory and experiment by the use of Eq. (1).

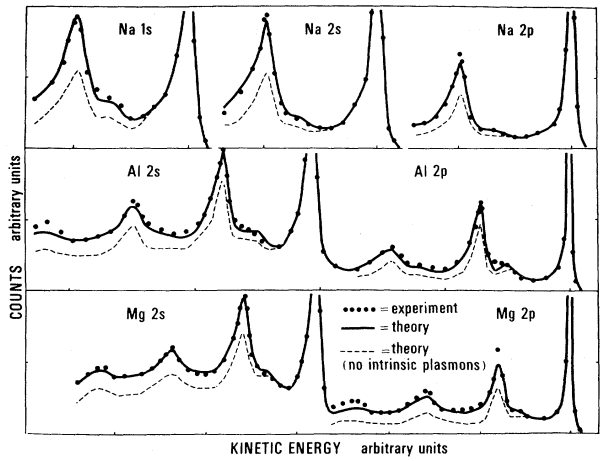

FIG. 1. Electron flux vs energy. The dots denote the experimental spectrum, the solid line is the theory, and the dashed curve is the theory without intrinsic plasmons. The highest peaks represent the no-loss lines; the loss peaks are at lower kinetic energy. The small bump between the no-loss peak and the first loss peak is caused by energy loss to surface plasmons.

The precise reason why neglect of the interference effect leads to such good agreement is not clear at present and is currently under investigation. Until this point is clarified, it might be prudent to regard my calculation of the intrinsic plasmon contribution to the first loss peak as somewhat tentative. I find it to be 26%, 36%, and 41% for Al, Mg, and Na, respectively. Nevertheless, it should be emphasized that the same estimates are obtained by comparing the experimental spectra of Fig. 1 (dotted curves) with the predicted spectra in the absence of intrinsic plasmons (the dashed curves in Fig. 1). Thus the latter estimates rely on the calculation of the loss spectra due to extrinsic processes as presented in sections (b) and (c) and not directly on the validity of Eq. (1).

For free-electron–like solids, $\mathrm{Im}(1/\epsilon)$ is nonzero for two distinct regions of q space: a region corresponding to creation of electron-hole excitations and a region corresponding to plasmon creation. In the electron-hole region ϵ in Eq. (1b) is taken to be the Lindhard dielectric function, while in the plasmon region I use the one-pole approximation

$$\mathrm{Im}[1/\epsilon(q,\omega)] = \omega_p^2\omega\tau_q/[(\omega^2-\omega_q^2)^2+(\omega\tau_q)^2], \qquad (2)$$

where $\hbar\omega_q$ is the plasmon energy and τ_q is a measure of the plasmon broadening.

For an unscreened core hole, $V_q = v_q$, but V_q can be estimated from experiment by assuming $V_q = \gamma v_q$ where γ is a constant to be determined. Equation (1b) then yields an almost constant value of $\alpha(\omega)$ for $\hbar\omega \leq \epsilon_F$ where ϵ_F is the Fermi energy. This agrees with work by Minnhagen and implies[5] that $\alpha(\omega=0)$ equals the experimentally measured singularity index α^{expt}. Setting $\alpha(0)=\alpha^{\mathrm{expt}}$ determines the constant γ and consequently $\alpha(\omega)$ for all ω. γ is found to be 0.89, 0.88, and 0.91 for Al, Mg, and Na, respectively. In principle, γ is a function of q and the validity of assuming γ to be constant has been verified by repeating the Al $2p$ and Na $2p$ calculations using the expression for V_q determined by Minnhagen.[5]

The portion of the experimental loss spectra due to surface plasmons is small as can be seen from Fig. 1. Because intrinsic surface plasmons are expected to comprise only a fraction of the surface-plasmon loss peak, I felt their contribution to the loss spectra did not warrant the effort required to include them in the calculations and they have therefore been neglected.

(b) *Transport to the surface:* This is described by the transport equation

$$\frac{\varphi(E)}{l(E)} = s(E) + \int_E^\infty dE'\varphi(E')v(E')^{-1}P(E',E), \qquad (3a)$$

where $\varphi(E)$ is the electron flux, $P(E,E')$ is the probability per unit time that an electron is scattered from E' to E, and $v(E)$ is the velocity of an electron of energy E. The electron mean free path, l, is given by

$$l(E)^{-1} = v(E)^{-1}\int_{\epsilon_F}^{E} dE'P(E,E'). \qquad (3b)$$

Equation (3) is derived from a transport equation used by Wolff[9] to account for multiple inelastic scattering and follows from Eq. (5) of Wolff and the following assumptions: (i) a steady state; (ii) that φ is spatially uniform inside the solid (this follows because l is in the range 20–40 Å, which is very short compared to the x-ray penetration depth but sufficiently large that the effect of the surface on φ inside the solid can be neglected); and (iii) that the electron scattering is primarily forward at high energies. Ritchie *et al.*[10] and Langreth[11] have used equations that are equivalent to Eq. (3).

Equation (3a) states that the rate electrons are scattered out of the state with energy E is equal to the rate they are photoexcited into E plus the rate they are scattered into E from higher-energy

states. The integral Eq. (3a) can be solved numerically for φ, once s and P are determined. For free-electron–like materials,

$$P(E,E') = \frac{v(E)}{\pi a_0 E}\int\frac{dq}{q}\mathrm{Im}\left[\frac{1}{\epsilon(q,E-E')}\right], \tag{4}$$

where a_0 is the Bohr radius. The core-electron contribution to l is determined by a method given by Powell.[12]

Equation (3) implies that the loss spectrum is essentially determined by $P(E,E')/\int_{\epsilon_F}^{E}dE''P(E,E'')$, so the error in the calculated satellite intensities caused by approximating ϵ will be small compared to the error in P which I estimate[13] to be on the order of 10% or less.

(c) *Escape through the surface:* The observed flux outside the solid, $S(E)$, differs from that inside the solid because of scattering by surface plasmons. $S(E)$ is given by

$$S(E) = \varphi(E)[1-p_T(E)] + \int_E^\infty dE'\varphi(E')[v(E')]^{-1}p(E',E), \tag{5a}$$

$$p_T(E) = \int_{\epsilon_F}^{E}dE'p(E,E'). \tag{5b}$$

Here $p_T(E)$ is the probability that an electron of energy E is scattered by a surface plasmon as it passes through the surface, and $p(E',E)$ is the probability that an electron is scattered from energy E' to E (under the assumption of forward scattering). Equation (5) states that the flux outside the surface at energy E is equal to the flux inside at E times the probability that these electrons pass through the surface without scattering plus a term which represents the flux scattered into the state E from higher-energy states.

The quantity $p(E,E')$ is obtained directly from an expression for the self-energy of an electron in the presence of the surface.[14] The result of the calculation[15] is

$$p(E,E') = (\tfrac{1}{2}\pi^2 a_0 E)^{-1}\int dq\, q^{-2}\int_0^{2\pi}d\varphi'\psi(q,\varphi',E,E')\,\mathrm{Im}[1+\epsilon]^{-1}, \tag{6a}$$

$$\psi(q,\varphi',E,E') = [1-(\sin\theta\sin\delta\cos\varphi'+\cos\theta\cos\delta)^2]^{1/2}, \tag{6b}$$

$$\cos\delta = \frac{(E-E'-\hbar^2q^2/2m)}{2q\sqrt{E}(\hbar^2/2m)^{1/2}}, \tag{6c}$$

where θ is the angle between the direction the electron is moving and the surface normal. In Eq. (6a) $\mathrm{Im}[1+\epsilon]^{-1}$ is approximated by the one-pole expression of Eq. (2) with ω_p^2 replaced by $\frac{1}{2}\omega_s^2$ where $\hbar\omega_s$ is the surface-plasmon energy. This approximation satisfies the surface sum rule.[16] In the case of an electron traveling in a direction normal to the surface ($\theta = 0$), neglecting q^2 in Eq. (6) and using the one-pole approximation result in the semiclassical expression derived by Ritchie.[17] Thus Eq. (6) is the quantum-mechanical version of Ritchie's expression generalized to all values of θ. Numerical evaluation of Eq. (6) gives the result $p(E',E;\theta)\simeq p(E',E;\theta=0)/\cos\theta$.

Input parameters.—The no-loss line shapes, $s(E)$ for $E > E_0 - \frac{1}{2}\hbar\omega_p$, are taken directly from the experimental data of McFeely and Kowalczyk[18] for Al and Mg, and Citrin, Wertheim, and Baer[19] for Na. The singularity indices are determined by Citrin, Wertheim, Baer[20] to be 0.118, 0.135, and 0.201 for Al, Mg, and Na, respectively. The bulk-plasmon energies are[21,22] 15.0, 10.8, and 5.69 eV for Al, Mg, and Na, respectively. The bulk-plasmon dispersion is obtained from $\mathrm{Re}[\epsilon(q,\omega)] = 0$ where the Lindhard dielectric function ϵ is evaluated at an electron density appropriate to the observed plasmon energy. The width of the bulk plasmon is[21,23,24]: $\Gamma_{Al} = 0.9 + 1.33q^2$, $\Gamma_{Mg} = 0.95 + 1.45q^2$, and $\Gamma_{Na} = 0.4 + 2q^2$ where Γ is in electron volts and q is in units of the Fermi momentum. From Ref. 12 and optical data,[21] the core-electron contribution to the mean free path is 16%, 22%, and 36% for Al, Mg, and Na, respectively.

Since the XPS experiments were carried out on evaporated films, it is not clear what choices to make for the surface parameters; fortunately, surface-plasmon losses are a small fraction of the loss spectrum. From inelastic low-energy electron diffraction,[25] the surface-plasmon dispersion and broadening for Al(111) are $\hbar\omega_s = 10.5 + 3.4q_\parallel$ and $\Gamma_s = 1.85 + 5.1q_\parallel$ and I use these values. For Mg, I use $\hbar\omega_s = \hbar\omega_p^{Mg}/\sqrt{2} + (\epsilon_F^{Mg}/\epsilon_F^{Al})3.4q_\parallel$ and $\Gamma_s = 1.4 + (\epsilon_F^{Mg}/\epsilon_F^{Al})5.1q_\parallel$, where the value 1.4 is obtained from optical data.[21] In the case of Na, any "sensible" estimate of $\hbar\omega_s$ and Γ_s produces a theoretical surface-plasmon peak that is

much larger than that actually observed. This discrepancy is probably due to a very small and unavoidable contamination of the Na surface by oxygen.[26] In order to obtain a resonable fit to experiment the electron–surface-plasmon coupling was arbitrarily reduced by a factor of 2.5.

For Al $2p$ an increase of 10% in the bulk- and surface-plasmon broadening as well as in α results in a decrease in R = (height of first loss peak)/(height of no-loss peak) of less than 1% and an increase in the intrinsic plasmon contribution to the first loss peak to 0.29 from 0.26 while the same increase of the plasmon broadening and a decrease of 10% in α results in a decrease in R of 7% and a decrease in the intrinsic plasmon contribution to the first loss peak to 0.23.

The results of the calculation are compared to experiment in Fig. 1. The good agreement between theory and experiment attests to the validity of the transport equation,[9-11] Eq. (3), in describing the energy losses due to extrinsic processes. It also lends support to the theory of intrinsic plasmon production as presented in Ref. 6 by Langreth.

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