Analysis of surface- and bulk-plasmon contributions to x-ray photoemission spectra

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The plasmon structure accompanying core-level x-ray photoemission in Na, Mg, and Al is reported and analyzed using a model of random *spatial* emission of extrinsic plasmons. The Mg and Al spectra are well fit by this model without intrinsic plasmon production. The Na data are not explained by purely extrinsic plasmon emission.

X-ray photoemission spectroscopy (XPS) provides a new method for studying energy-loss structure associated with electrons travelling through solids. The XPS spectra differ in two important respects from spectra generated by transmission of electrons through thin films. First, in XPS the x-ray beam penetrates thousands of angstroms; therefore, photoemission occurs, and full-energy electrons originate, essentially uniformly through the first few-hundred angstroms that form the effective source. Second (and of more theoretical interest), XPS provides the possibility of observing intrinsic, as well as extrinsic, plasmon structure. As spectrometer resolution and sample preparation techniques improve, XPS spectra are yielding continually more striking plasmon structure. A recent survey described energy-loss structure, including surface- and multiple-bulk plasmons, in XPS spectra of several metals.[1] The analysis of relative intensities in that work was rather emprical, and it did not explicitly consider certain statistical aspects of multiple plasmon formation.

Recent interest in the possiblity of observing intrinsic plasmons in free-electron-like metals by XPS has inspired the present collaboration. This type of plasmon excitation is intrinsic to the photoemission of a core electron that is coupled with the surrounding plasma and differs from an extrinsic plasmon which is produced by a nearly free electron which is coupled by its longitudinal electric field to electron density fluctuations while it passes through a solid. Although intrinsic and extrinsic plasmon emission produce lines at the same series of energies, their relative contributions to successive lines is different, permitting their separation. In this paper we report a careful analysis of experimental x-ray photoemission spectra into surface- and bulk-plasmon components. We consider specifically data for the Na 2*s*, Mg 2*s*, and Al 2*s* lines, all obtained under ultrahigh-vacuum conditions. The Na data were reported previously,[2] while the Mg and Al data are new. Not only the zero plasmon line, but also the first few bulk plasmon lines are found to have appreciable surface plasmon satellites. These extrinsic plasmon effects constitute 90% of the observed loss structure in Al and Mg, with the remainder apparently due to other inelastic effects, *not including* intrinsic plasmons. The Na spectrum, in contrast, cannot be explained by purely extrinsic plasmon effects, and qualitatively suggests a combination of intrinsic and extrinsic effects. However, we found that even this did not quantitatively explain the observed spectrum.

The background on the low-binding-energy side of the 2*p* zero-loss peak was taken in each case as the starting point for the background correction. It was assumed that a flat background of this intensity lay under both the 2*p* and the 2*s* loss spectra. The 2*s* loss spectra were then corrected for the tail of the 2*p* loss structure, which extends into the 2*s* region, as illustrated in Fig. 1. This correction was significant for Mg and Al, but not for Na.

After background corrections were made, the 2*s* zero-loss peak P_0, the first bulk plasmon peak P_1, and the first surface plasmon peak S_1 were separated graphically. Then a series of high-order bulk plasmon peaks was obtained by convolution. For example, the energy distribution $P_2(E)$ of photoelectrons which have created two bulk plasmons is[3,4]

$$P_2(E) = \int dE'\, P_1(E')P_1(E - E') \equiv (P_1 \times P_1)(E) . \quad (1)$$

In general,

$$P_n(E) = (P_{n-1} \times P_1)(E) . \quad (2)$$

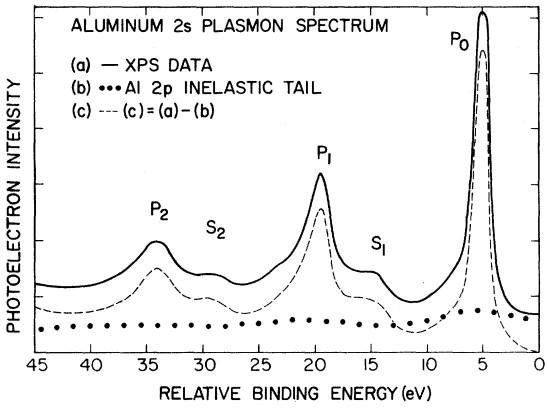

FIG. 1. Aluminum 2*s* plasmon spectrum (a) solid line, XPS data; (b) dots, Al 2*p* in elastic tail; (c) dashes, XPS data minus Al 2*p* inelastic tail.

Each bulk plasmon peak has a surface plasmon satellite, again generated by convolution,

$$S_n(E) = (P_{n-1} \times S_1)(E) \ . \tag{3}$$

Analysis is facilitated by adding each bulk plasmon peak to its surface plasmon satellite. For example,

$$R_1 = P_1 + S_1 , \tag{4}$$

$$R_n = P_n + S_n . \tag{5}$$

The relative weights of the R_n were varied to yield good visual fits to the data. The results for the Al 2*s* level, exhibiting the individual surface and bulk plasmon components are shown in Fig. 2. Figures 3 and 4 show the generated and experimental spectra for Mg and Na, respectively.

We use Mahan's model[4] of random *spatial* emission of extrinsic plasmons. That is, the average

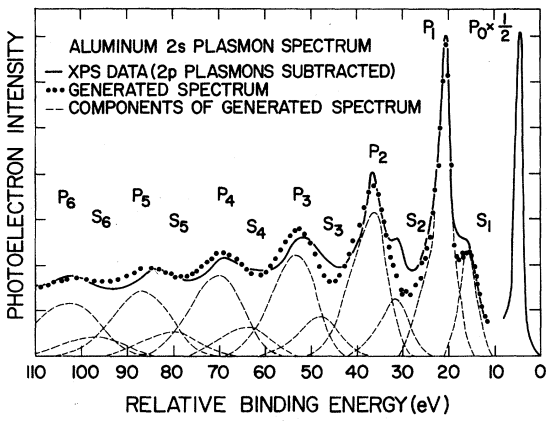

FIG. 2. Aluminum 2*s* plasmon spectrum: solid line, XPS data (2*p* plasmons subtracted); dots, general spectrum; dashes, components of generated spectrum.

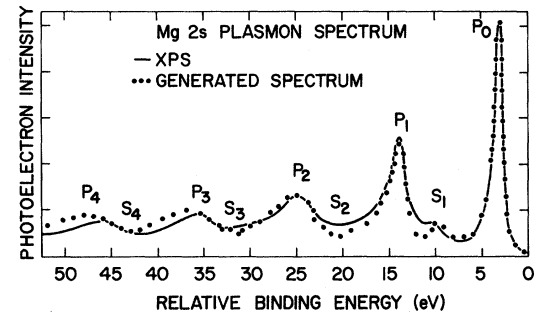

FIG. 3. Magnesium 2*s* plasmon spectrum (a) solid line, XPS data and (b) dots, generated spectrum.

number of (extrinsic) bulk plasmons produced by a photoelectron originating at a depth z is $Q(z) \simeq z/l$, where l is the mean free path for plasmon emission. The probability of creating n bulk plasmons by a (fast) photoelectron originating at a depth z is then

$$P(n, z) = \exp(-z/l)\,(z/l)^n/n! \ . \tag{6}$$

We remind the reader that this is the probability of finding n randomly distributed points with mean separation l in a distance z. It is not equivalent to a Poisson distribution of the spectral intensities. In fact, since the penetration depth of the x-rays is orders of magnitude greater than l, the total probability of n bulk plasmons is proportional to

$$P(n) = \int_0^\infty dz\, P(n, z) = l , \tag{7}$$

independent of n. We find, however, that the area ratio

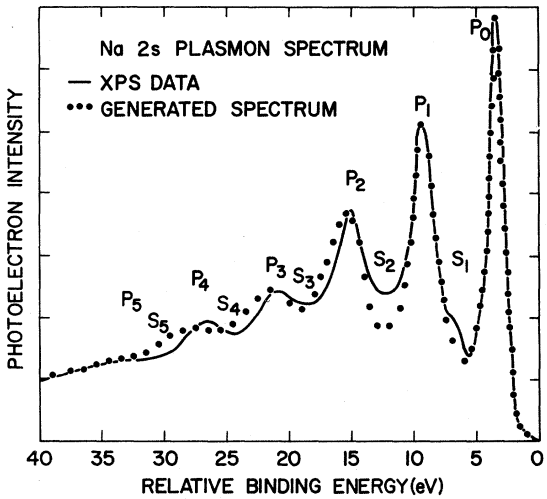

FIG. 4. Sodium 2*s* plasmon spectrum (a) solid line, XPS data and (b) dots, generated spectrum.

$$A_n = \int dE\, R_n(E) \Big/ \int dE\, R_0(E) \tag{8}$$

decreases slightly with n. This can be understood if we recognize that there exist other loss mechanisms which can remove electrons from the observed spectrum. For example, the photoelectron can eject a $2p$ electron with neither being detected. If these processes have a mean attenuation length L, then the probability of an electron originating at depth z, emitting n bulk plasmons, and not being removed by these other processes, is

$$P(n, z) = e^{-z/L} e^{-Q} Q^n / n! \ . \tag{9}$$

This implies

$$P(n) = l/(1 + l/L)^{n+1}, \tag{10}$$

so the area ratios should decrease geometrically with n.

Intrinsic plasmon spectra, in contrast, have the *area ratios*, rather than spatial emission, Poisson distributed[5]

$$P(n) = e^{-\beta} \beta^n / n! \ . \tag{11}$$

The combined effects of intrinsic and extrinsic emission and the other inelastic effects are easily obtained from Langreth's work[6] (although the physics is slightly different)

$$A_n = \alpha^n \sum_{m=0}^{n} \frac{(\beta/\alpha)^m}{m!} \ . \tag{12}$$

The parameter α is here the inelastic loss factor $\alpha = (1 + l/L)^{-1}$.

The fits for the Mg $2s$ and the Al $2s$ loss structures have precisely the behavior of Eq. (10), with $\alpha = 0.9$, or $L \cong 10l$. On this basis we suggest that extrinsic plasmon production represents 90% of the loss structure. The constancy of A_n/A_{n-1} implies β/α is $\ll \frac{1}{10}$. Intrinsic plasmon production ($\beta \neq 0$) would not permit us to fit the data with Eq. (10). This is the case for Na, in which the area ratios A_n are $A_0 : A_1 : A_2 : A_3 : A_4 : A_5 : A_6 =$ 1 : 1.05 : 1.1 : 0.8 : 0.65 : 0.45 : 0.4. Neither, however, are they quantitatively fit by Eq. (12), although it at least permits the maximum of A_n to occur at $n > 0$. It may be that the background is not flat as assumed, perhaps containing contributions from diffuse intrinsic plasmons.

The average number of surface plasmons produced in Na, Mg, and Al were, respectively, 0.25, 0.273, and 0.31. These are somewhat larger than the theoretical estimate[4,5]

$$Q_s \simeq e^2/(2\hbar v) \simeq 0.15 \ . \tag{13}$$

We note that for Al, $Q_s^2/2! \simeq 0.05$, so processes involving two surface plasmons constitute a barely visible 5% effect. These occur as a series of peaks centered at $n\hbar\omega_B + 2\hbar\omega_s$. In Al these peaks should fall at 25.3, 40.9 eV, etc., from the main peak. We see (Fig. 2) that at these energies the generated spectrum has, indeed, fallen perceptibly below the experimental spectrum.

The random-spatial-emission model is not universally accepted.[6] Perturbation theory arguments in momentum space[7] give, in contrast to Eq. (7),

$$P(n) = \alpha^n, \tag{14}$$

with $\alpha \cong \frac{1}{2}$. This is too small to fit the data, but is similar in form to Eq. (10). Chang and Langreth have shown that Eq. (14) follows from a classical picture of independent emission in time. In particular, they assume a sharp plasmon can be emitted in the length of time it takes the electron to cross an atomic layer. But for the electron to change its energy by, say, 10 eV, requires a time $\Delta T \sim \hbar/10$ eV $= 6.6 \times 10^{-17}$ sec, while a 1.5-keV electron crosses 4 Å in $T \cong 1.7 \times 10^{-17}$ sec, a factor of 4 too small. The requirement that the plasmon be sharp makes ΔT a factor of 10 larger, or comparable to the entire time the electron spends in the solid. Independent spatial emission does not encounter this difficulty. Of course the failure of the classical derivation does not mean the result Eq. (14) is wrong.

In summary, the XPS data for the Al and Mg $2s$ lines were found to be dominated by a series of extrinsic plasmon lines, each bulk plasmon line having a surface plasmon satellite. The ultrahigh-vacuum conditions permitted the production of relatively large numbers of surface plasmons, with processes involving two surface plasmons discernable. For Al and Mg the decrease of A_n with n suggests a mean attenuation length due to other inelastic processes of $L \simeq 10l$. Intrinsic plasmon production seems negligible for these two spectra. The Na data was similar, but with indications of intrinsic plasmon (plasmaron) production. The picture of independent spatial emission of the extrinsic plasmons is supported by these results.

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[1]R. A. Pollak, L. Ley, F. R. McFeely, S. P. Kowalczyk, and D. A. Shirley, J. Electr. Spectrosc. 3, 381 (1974).

[2]S. P. Kowalczyk, L. Ley, F. R. McFeeley, R. A. Pollak, and D. A. Shirley, Phys. Rev. B 8, 3583 (1973).

[3]M. Sunjic and D. Sokcevic, Solid State Commun. 15, 165 (1974); and D. Sokcevic and M. Sunjic, *ibid.* 15, 1703 (1974).

[4]G. D. Mahan, Phys. Status Solidi B 55, 703 (1973).

[5]J. J. Chang and D. C. Langreth, Phys. Rev. B 8, 4638 (1973).

[6]D. C. Langreth, in *Collective Properties of Physical Systems*, edited by B. Lundquist and S. Lundquist (Academic, New York, 1974).

[7]J. J. Chang and D. C. Langreth, Phys. Rev. B 5, 3512 (1972).