Determination of Surface-Plasmon Dispersion Relation by Ricochet Photoemission

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(Received 20 February 1986)

Photoelectrons emitted along a metal surface from atoms located at a small distance outside that surface have a high probability to ricochet with the excitation of a surface plasmon if the angle of emergence α is less than a critical angle α_M. The line shape of the surface-plasmon satellite $I_1(\varepsilon_k,\alpha)$ peaks strongly at $\alpha=0$ and presents another peak at $\alpha=\alpha_M$. Experiments are suggested to locate the second peak and thereby determine $\alpha_M(\varepsilon_k)$, a function which should yield direct information on the form and the parameters of the surface-plasmon dispersion relation.

PACS numbers: 79.60.Cn, 71.45.Gm, 79.60.Gs

It is well known that the intensity of x-ray photoemission (XPS) of a metal with surface-plasmon (SP) production increases strongly as the angle of emergence α, i.e., the angle between the direction of exiting photoelectron and the metal surface tends to zero.[1,2] *Theoretically*, this situation corresponds to a logarithmic α divergence in the calculation if appropriate cutoffs are not introduced. *Experimentally*, a vanishing α with meaningful results is difficult to realize, when the photoemitting atom (metal ion or impurity atom) is located *inside* the metal. However, in a previous paper[3] (hereafter referred to as I), we have suggested an experiment where the atom is located just outside the metal at a small distance z_0 from the surface and where emergence angle $\alpha=0$ can be realized. We have shown that a cutoff can be introduced in the calculation if the distance l traveled by the photoelectron along (but outside) the metal surface is considered finite. The total photoemission intensity of SP production is then logarithmically dependent on l/z_0 for α less than a small critical angle $\alpha_M \approx (\omega_s/\omega_0)^{1/2}$ where ω_s is the SP energy and ω_0 is the initial energy in the photoproduction process (x-ray photon energy minus extraction energy). For $\alpha > \alpha_M$ no cutoff is required. We showed that for an initial excitation energy, say $\omega_0=1.4$ keV and $\omega_s=11$ eV (SP frequency for Al), α_M would be of the order of a few degrees, and suggested that a successful experiment could be performed for $7\ \text{Å} < l < 10$ cm.

In this Letter, we introduce the SP dispersion (disregarded in I) and present the theory of the SP-loss intensity I_1 as a two-variable function depending on angle α and energy $\varepsilon_k=k^2/2m$ of the outgoing photoelectron. We show that the XPS with grazing emergence presents a structure which is able to give exceptional information regarding the exact form of the SP dispersion relation. In particular, we show that intensity $I_1(\varepsilon_k,\alpha)$ has a maximum at $\alpha \approx \alpha_M$ which should be detectable in an XPS experiment and from which the SP dispersion relation can be obtained.

A general SP dispersion relation can be written in the form

$$\omega_s(q)=\omega_s^0+\beta q^n, \tag{1}$$

where ω_s^0 is usually related to the bulk-plasmon frequency ω_p (at zero momentum) by $\omega_s^0=\omega_p/\sqrt{2}$. Generally this dispersion rule is considered linear ($n=1$) as in the well-known hydrodynamic model[4] where $\beta=(\frac{3}{5})^{1/2}v_F/2$ (v_F is the electron velocity at the Fermi level). However, other dispersion relations have also been suggested (not necessarily linear). They depend not only on the theoretical model but also on the physical state of the surface, a point which presents an obvious technological interest such as characterization of the surface. Up to now no experiment seems to have been available which would yield direct information on the dispersion rule. In the present Letter we show that the XPS experiment with quasiparallel emergence can precisely yield information about the parameters β and n appearing in (1). In Figs. 1(b) and 1(c) we propose two experimental setups which can be used to obtain direct information about the surface-plasmon dispersion relation. Such experimental setups should be particularly interesting since, in principle, only surface excitations should be observed here, unlike most x-ray or electron spectra experiments where effects of SP are weakened or obliterated by other effects (such as main-line tailing, bulk plasmons, etc.). Indeed, once the photoelectron penetrates into the metal, it will have a high probability of being trapped inside, especially if z_0/l is small or the metal sample is prolonged by an absorbent material [see Fig. 1(a)].

Let us represent by $I_0(\varepsilon_k)$ and $I_1(\varepsilon_k,\alpha)$ the intensities of photoemission without and with one SP loss, respectively. The intensity $I_0(\varepsilon_k)$ which is isotropic can be written as $I_0(\varepsilon_k)=\delta(\omega_0-\varepsilon_k)$. Using the same normali-

zation we will write

$$I_1(\varepsilon_k,\alpha)=(2\pi)^{-2}\int d^2q\,\delta(\omega_0-\varepsilon_k-\omega_s(q))\,|M|^2. \tag{2}$$

Referring to Fig. 1(a), we can write the matrix element as

$$M=\frac{1}{(2\pi)^3}\left[\frac{\omega_s(q)\pi e^2}{q}\right]^{1/2}\int d^3x\,\theta(z)\int d^3p\frac{\exp[-i\mathbf{p}\cdot\mathbf{x}_0+i(\mathbf{p}-\mathbf{k}-\mathbf{q})\cdot\mathbf{x}-qz]}{\omega_0-\varepsilon_p+i\lambda}. \tag{3}$$

Points $\mathbf{x}_0=(0,0,z_0)$ and $\mathbf{x}=(x,y,z)$ are sites of photoemission and SP excitation, respectively. The metal is located in the region $z<0$ and $x<l$. In our proposed experimental devices, interaction with the SP potential occurs only outside the metal, i.e., for $z>0$ (otherwise the electron will be trapped inside the metal) and for $x<l$. The first condition is introduced by the step function $\theta(z)$ in (3). Another step function $\theta(l-x)$ should also be present. However, we showed in I that the effect of this latter cutoff could equivalently be incorporated into (3) by the small but finite quantity $\lambda=1/2t=k_\parallel/2ml$ in the denominator, where t is the time of flight of the photoelectron to reach the edge region at $x=l$. All the integrals in (3) can be performed analytically and one obtains

$$|M|^2=\frac{\pi e^2 m\,\omega_s(q)}{2q\,|q+ik_z+i(2mv)^{1/2}|^2}\frac{\exp[-2z_0(2m)^{1/2}\mathrm{Im}(v+i\lambda)^{1/2}]}{(v^2+\lambda^2)^{1/2}}, \tag{4}$$

with $|\mathbf{k}_\parallel|=k\cos\alpha$, $k_z=k\sin\alpha$, and $v=\omega_0-|\mathbf{k}_\parallel+\mathbf{q}|^2/2m$. If we neglect terms of order $(z_0/l)^2$, the second fraction of (4) can be simplified as $\theta(v)\times\exp[-z_0\lambda(2m/v)^{1/2}]/v$.

A glance at (3) shows that λ plays a significant role only when $\omega_0\approx\varepsilon_p$ or, in other words, when a strict conservation of energy occurs in the virtual state between the two processes of photoemission and SP excitation. Such a conservation can hold only if the interaction with the SP field lasts for a sufficiently long time. In fact this does not happen in a usual XPS experiment when α is far from zero. In that situation the photoelectron spends only a short time in the SP-field region and λ can then be set equal to zero in (3), giving an intensity I_1 independent of t (or equivalently of l). Further insight into the SP problem can be obtained if we compare it with the excitation of a *bulk* plasmon by a photoelectron created *inside* a metal sample. The rate of *single* bulk-plasmon production can be calculated from expressions rather similar to (2) and (3). However, here the time t of interaction with the bulk-plasmon field is long—as long as the photoelectron travels inside the metal. Thus, strict conservation of energy $\omega_0=\varepsilon_p$ (with $\mathbf{p}=\mathbf{k}+\mathbf{q}$) occurs in the intermediate (real) state, and λ cannot be ignored. But here the calculations are much more straightforward than for the present SP case. A factor $[(\omega_0-\varepsilon_{|\mathbf{k}+\mathbf{q}|})^2+\lambda^2]^{-1}$ appears in $|M|^2$. This factor becomes $2\pi t\,\delta(\omega_0-\varepsilon_{|k+q|})$, yielding the well-known linear dependence on t of the *single* bulk-plasmon production.

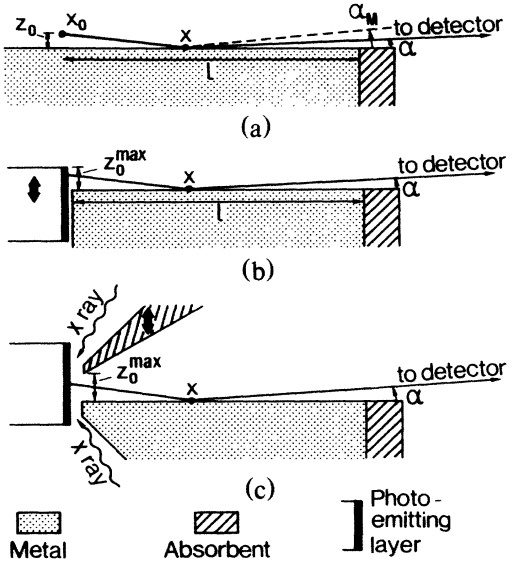

FIG. 1. (a) The process of ricochet photoemission. The photoelectron is created at $\mathbf{x}_0$ and it interacts with the SP field at $\mathbf{x}$. The line shape $I_1(\varepsilon_k,\alpha)$ will have a maximum at $\alpha=\alpha_M$. (b),(c) Possible experimental setups to observe ricochet photoemission. A photoemitting layer is placed next to the metal sample and $z_0^{\max}$ can be controlled and altered by means of movable parts (double-thick arrows). These figures are schematic and do not respect angles and proportions.

Equation (4) for the SP case is slightly more complicated, however. The requirement of a nonvanishing λ occurs when

$$v\equiv\omega_0-|\mathbf{k}_\parallel+\mathbf{q}|^2/2m=0; \tag{5}$$

otherwise a logarithmic divergence in λ (or in t, or in l) will occur. In I, the main question treated was, "In what geometrical circumstances has a finite value to be assigned to λ in (3) or (4)?" and the answer was in the evaluation of α_M. In the present paper we are interested in the line shape and detailed angular dependence of $I_1(\varepsilon_k,\alpha)$, especially in and around the region of the (ε_k,α) space where $v=0$. A more precise answer has thus to be given which requires the delimitation of the region defined by (5).

Before proceeding any further we can make a few comments. Equation (5) looks like the condition of energy

conservation in the intermediate state in the bulk-plasmon production process; with a difference, however, since momentum conservation holds only in the plane parallel to the metal surface. To interpret (5), it is interesting to go back to a classical picture where energy conservation strictly holds in the intermediate state. Relation (5) then appears as the combination of two conditions: the above conservation of energy in the intermediate state $\omega_0 = p^2/2m = (p_z^2 + |\mathbf{k}_\parallel + \mathbf{q}|^2)/2m$, accompanied by the additional condition $p_z = 0$. In the classical scheme, a vanishing p_z means that the initial trajectory of the photoelectron is practically parallel to the surface, a condition which optimizes its interaction with the SP field. The electron will ricochet along the metal surface. The complementary insight comes from the actual quantum scheme where the photoelectron is described by a spherical wave centered at $\mathbf{x}_0$, and p_z is in fact undetermined. The region where an SP can be excited is the region of intersection of this wave with the region of the SP field, i.e., a flat disk centered at point **0**, of radius l and thickness q^{-1}. The probability of finding the electron inside that disk is thus proportional to

$$\int d^3x\,(z_0^2 + r^2)^{-1} = \pi q^{-1} \ln(1 + l^2/z_0^2)$$

and hence to $2\pi q^{-1}\ln(l/z_0)$ when l/z_0 is large. This latter condition, $l/z_0 \gg 1$, is obviously consistent with the classical condition $p_z \approx 0$ required for an efficient ricochet interaction with the surface.

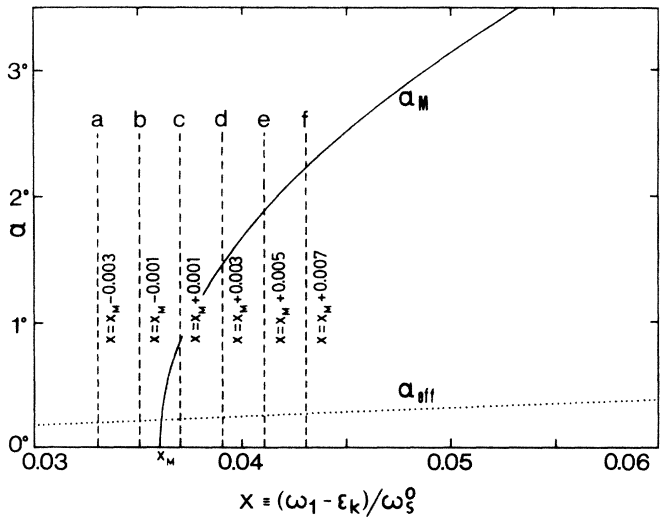

FIG. 2. Intensity I_1 of photoemission with SP loss depends on emergence angle α and energy ε_k of the outgoing photoelectron. This figure represents the space of α and ε_k variables (x is directly related to ε_k). Below the dotted curve $\alpha = \alpha_{\text{eff}}(x) = (q/k)^2$, I_1 peaks strongly. It depends logarithmically on l below solid curve $\alpha = \alpha_M(x)$ and presents a second peak along the curve. Above it I_1 collapses rapidly. The vertical dashed lines are related to Fig. 3.

Going back to (5) we note that it holds for

$$k_\parallel - q < (2m\omega_0)^{1/2} < k_\parallel + q. \tag{6}$$

The first inequality is always satisfied since $k_\parallel < k < (2m\omega_0)^{1/2}$ but the second one is crucial. Since q is determined by both the energy conservation for the whole process, i.e., $\omega_0 - \varepsilon_k - \omega_s(q) = 0$ [see (2)], and by the SP dispersion relation (1), let us write $q = (x\omega_s^0/\beta)^{1/n}$ with $x \equiv (\omega_1 - \varepsilon_k)/\omega_s^0$, a quantity which will be used hereafter instead of k or ε_k (it represents the energy of the photoelectron measured from the edge of the SP excitation $\omega_1 = \omega_0 - \omega_s^0$ in ω_s^0 units). Then let us write (6) as $\alpha < \alpha_M(x)$. Figure 2 shows the region of (x,α) space where this inequality holds (for $n = 1$ and β defined in the hydrodynamic model applied to Al). For x and α small,

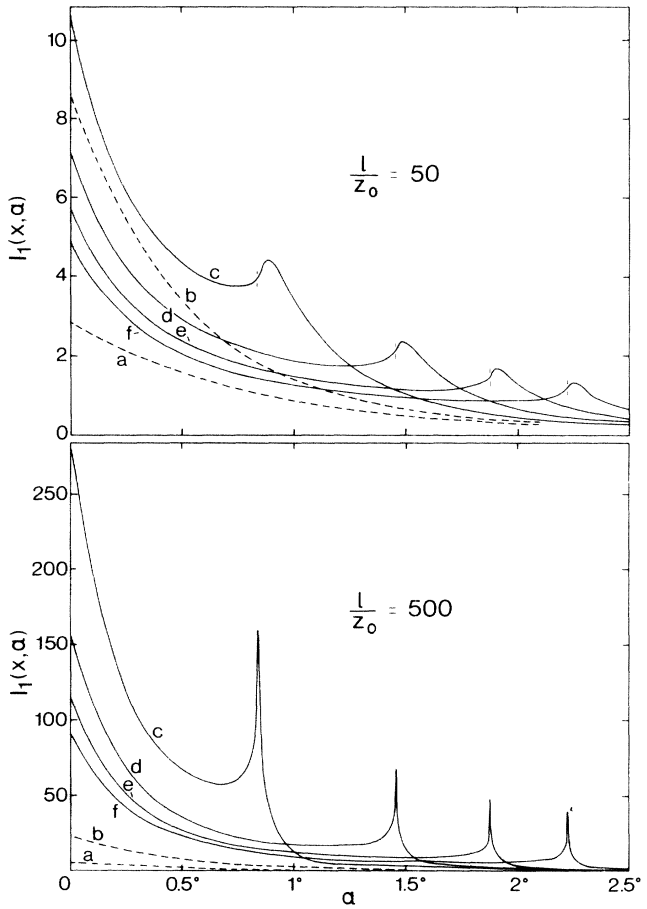

FIG. 3. Intensities $I_1(\varepsilon_k,\alpha)$ for $l/z_0 = 50$ and 500. The curves correspond to cuts in (x,α) space represented by dashed vertical lines of Fig. 2 with the same labels. Each curve is thus related to a particular value of x (or ε_k). Note the secondary peak appearing at $\alpha = \alpha_M$ beyond which the intensity collapses. The intensity also collapses for $x < x_M$ (curves a and b). The vertical scale corresponds to a normalization where $I_0(\varepsilon_k) = \delta(\omega_0 - \varepsilon_k)$ (zero loss intensity). Note the important differences on the vertical scales.

i.e., when I_1 is the largest, one has $\alpha_M(x) \approx [c(x/x_M - 1)]^{1/2}$, with $c = \omega_s^0/n\omega_0$, $x_M = \beta q_M^n/\omega_s^0$, and $q_M = \omega_s^0(m/2\omega_0)^{1/2}$ (x_M and q_M are the minimum values for x and q in that region). Function $\alpha_M(x)$ is then represented by a simple parabola and its experimental determination will yield direct information on the three main parameters (ω_s^0, β, and n) which define the SP dispersion relation (1). [Note that even though the above relationship between $\alpha_M(x)$ and the parameters of the surface-plasmon dispersion relation is approximate, the solid curve in Fig. 2 has been plotted using their exact relationship.]

This requires the measurement of the intensity $I_1(x,\alpha)$. Since the shape of $I_1(x,\alpha)$ depends on $\ln(l)$ for $\alpha < \alpha_M(x)$, it seems at first sight that a geometrical variation of l would locate this region. However, this technique is probably too elaborate to be achieved experimentally. Fortunately, another feature of $I_1(x,\alpha)$ can be exploited to locate this region with precision. Right at the border of it, i.e., for $\alpha = \alpha_M(x)$, the dependence of I_1 on l becomes linear as can be seen from (4) where the denominator reduces to λ. This means that a peak should appear in $I_1(x,\alpha)$ along this border.

We have actually performed the complete calculations of $I_1(x,\alpha)$ numerically using (2) and (4). The results are shown in Fig. 3 for $l/z_0 = 50$ and 500. We have used $\omega_0 = 130\omega_s^0$ as in I. The curves representing $I_1(x,\alpha)$ are plotted for several values of x as a function α. They correspond to the dashed lines in the (x,α) space of Fig. 2. First, a main peak appears at $\alpha = 0$. This peak has already been discussed in I and is due to the Lorentzian character (in α) of the first fraction $1/(k_z^2+q^2)$ in (4) (if we assume $v \approx 0$). This function obviously peaks for $\alpha < \alpha_{\text{eff}} = (q/k)^2$ with a maximum at $\alpha = 0$. A second smaller peak appears at $\alpha = \alpha_M$ as expected from the above discussion. This is the peak that needs to be observed experimentally for a successful determination of the function $\alpha_M(x)$ and the ensuing parameters of the dispersion relation (1). Beyond this peak, the intensity $I_1(x,\alpha)$ collapses since we move out of the region of logarithmic and (at the border) linear l dependence. Figures 1(b) and 1(c) display two possible experimental setups which can be used to measure $I_1(x,\alpha)$ vs α for a given $x(\varepsilon_k)$. $I_1(x,\alpha)$ will show a peak at $\alpha_M(x)$ from which the nature and parameters of the SP dispersion relation (1) will be obtained.[5]

A comment should be made about the peak at $\alpha = \alpha_M(x)$. This peak appears right at the border between the region where the intermediate state is real (energy is conserved) and the region where the state becomes virtual (see Fig. 2). This peak is related to a similar bulk-plasmon structure appearing in the x-ray absorption spectra of metals. This structure was predicted by the authors[6] some years ago and indeed observed[7] at the predicted frequency.

In conclusion, in this Letter we have developed a theory of ricochet photoemission line shape $I_1(\varepsilon_k,\alpha)$ in the presence of a SP dispersion relation. Our theory predicts a second peak at a critical angle $\alpha_M(\varepsilon_k)$ which is directly related to the nature of the SP dispersion relation. We have also proposed two experimental setups which can be used to measure the peak at $\alpha_M(\varepsilon_k)$, thereby determining the actual form of the SP dispersion relation.

One of the authors (P.L.) is grateful to the Fonds National de la Recherche Scientifique, Belgium, and the Coopération Scientifique Internationale, Belgium, for financial support.

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[5]As shown in Fig. 3 (upper panel), for relatively large z_0, i.e., for relatively small l/z_0 ($=50$), the peak intensity is slightly shifted above $\alpha_M(x)$. However, this is not a hindrance to a sharp determination of $\alpha_M(x)$. In realistic experiments, like those proposed in Figs. 1(b) and 1(c) an integration over z_0 from 0 to $z_0^{\max}$ is actually observed. Thus in the observed peak, contributions from smaller z_0's will be dominant because of their stronger intensities, and for smaller z_0's the maximum occurs right at $\alpha_M(x)$ (see bottom panel of Fig. 3).

Note also that $\alpha_M(x)$ does not depend on the approximation (viz., a step function replaced by λ) made in (3) for the evaluation of the matrix element. In fact $\alpha_M(x)$ is calculated from (6) and (1), i.e., from the condition of divergence of (4). It thus depends only on the location of this divergence and not on the way the cutoff is introduced.

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