Collective and single-particle excitations in the photoyield spectrum of Al

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Using angle- and energy-resolved photoyield spectroscopy, we investigate the properties of the multipole plasmon excitation. At higher energies, a systematic dependence of the photoyield on the photon angle of incidence is observed and explained on the basis of classical Fresnel theory, indicating the possibility of obtaining information about optical constants from such measurements. A feature above the multipole plasmon is assigned to the excitation of a bulk plasmon by the photon field. [S0163-1829(98)51132-0]

Collective excitations are of fundamental importance for understanding the response of a metal to an incident electromagnetic field, and have attracted the attention of physicists over many years.[1] The collective excitations originate from the oscillatory modes of the surface electron density, which appear at the poles of the surface reponse function, and causes an enhancement of the photoemission intensity. These excitations occur below the bulk plasmon frequency (ω_p) where, due to the dynamic screening of the external field, the microscopic surface electric field varies rapidly and deviates appreciably from the classical Fresnel fields.[2] Above $\hbar\omega_p$ however, the surface becomes transparent to the incident radiation and the Fresnel equations are expected to be valid. Evidence for an increase in the total photoyield below $\hbar\omega_p$ was observed on thick alkali metal films in the early work of Monin and Boutry.[3] An enhancement of surface photoyield was also observed in Mg,[4] Al,[5] In,[6] Be,[7] and Na layers on Cu,[8] though most of the early studies suffered from problems of surface roughness and the total yield measurement technique. The advantage of angle- and energy-resolved photoyield (AERPY) over the total yield measurements is that it does not have contribution from the inelastically scattered secondary photoelectrons, which is difficult to analyze and may also depend on surface quality and sample preparation history. The first reliable study of collective excitations, using the AERPY technique, was performed by Levinson, Plummer, and Feibelman for Al(100).[9] They showed that there is a large increase in photoyield below ω_p, with a peak at a relative frequency of $0.8\omega_p$.[9,10] The experimental result could only be explained by calculating the photoemission matrix element explicitly, taking into account the variation of the electric field at the surface, which is generally neglected. Different theoretical studies[1,2,11–15] concerning the nature of the collective modes have been performed to explain the experimental data of Levinson, Plummer, and Feibelman. The $0.8\omega_p$ peak has been assigned to a multipole surface plasmon excitation.

Although in recent years there has been improvement in the predictive capability of theory,[1,16–19] a comprehensive experimental study of collective excitations on a metal surface using photons has been lacking. The advantage of using photons rather than electron-energy-loss spectroscopy,[20,21] (EELS) is that the dominant monopole surface plasmon mode is not excited by photons, and thus weaker surface modes (for example, the multiple mode) can be observed. Moreover, due to the finite detector aperture in EELS, the $q_{\parallel}=0$ multipole plasmon is mixed with the monopole plasmon mode.[22] In this paper, we report investigations of the photoresponse in Al(111) using AERPY spectroscopy. We examine the different types of collective excitations (including multipole plasmon and threshold excitations) that are already known to exist,[1,17,19] and present evidence for a collective excitation above $\hbar\omega_p$ at 16 eV. Furthermore, a single-particle excitation related feature above $\hbar\omega_p$ disperses systematically as a function of photon incident angle, and is explained by Fresnel theory. The agreement between experiment and calculation suggests the possibility of obtaining information about optical constants of surfaces using such techniques.

The measurements were carried out on the 1-m Seya-Namioka and toroidal grating monochromator (TGM4) beamlines at the Berliner-Elektronone-Speicherring-Gesellschaft für Synchrotronstrahlung (BESSY) storage ring using a commercial angle-resolving electron spectrometer (ADES400 from VG, U.K.) at a base pressure of 6×10^{-11} mbar. Electropolished Al(111) crystals were cleaned by repeated sputtering and heating cycles; a sharp (1×1) low-energy electron diffraction pattern was observed from the clean surface. The AERPY spectra were measured using *p*-polarized light by recording the intensity at the Fermi level (E_F) in the energy- and angle-resolved mode, to avoid contribution from the inelastically scattered electrons.[19] The data were collected in the normal emission geometry as a function of the angle of incidence (α), defined with respect to the sample normal (see inset of Fig. 1). Both the sample and the analyzer were rotated by the same angle

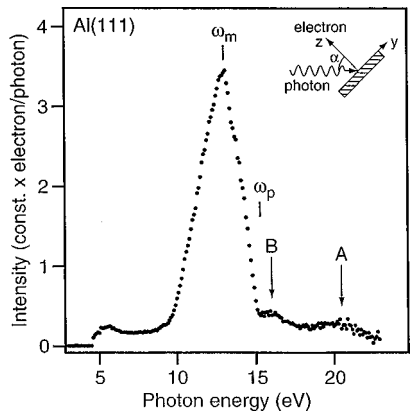

FIG. 1. Angle- and energy-resolved photoyield spectrum of Al(111) measured by the intensity at E_F in normal emission geometry with $\alpha=45°$. ω_m and ω_p correspond to multipole and plasmon frequencies, respectively. The measurement geometry is shown in the inset.

in order to change α, so that the normal emission collection geometry is unchanged. The plane of incidence was the mirror symmetry plane of the crystal, either along the 110 (Γ K) or 1 12 (Γ M) directions. In order to improve the quality of the data and to decrease the measuring time, the intensity at E_F was measuared in the constant initial state (CIS) mode at typical binding energies of 0.1 or 0.3 eV. Photoemission spectra were also recorded to confirm the CIS data. The data were normalized as described in Ref. 19.

A representative AERPY spectrum for Al(111), taken in the CIS mode at 0.1 eV binding energy, is shown in Fig. 1. The work function cutoff for the threshold of photoemission is observed at 4.5 eV. The peak at 13 eV is related to the excitation of the multipole plasmon that enhances the photoemission signal. The multipole plasmon decays by transferring its energy to electron-hole pairs.[23] A similar mechanism of plasmon decay has been suggested for Na clusters by Reiners *et al.*.[24] We have observed that there is an increase in the intensity of the entire photoemission energy distribution curve in the multipole plasmon region. This indicates that the electron-hole transitions occur from the entire valence band. The multipole peak has a triangular shape (full width at half maximum 3 eV) with a sharp increase in intensity below $\hbar\omega_p$ (at 15 eV for Al) and a relatively gradual decrease beyond the maximum. The large width of the multipole plasmon in Al is in agreement with the total photoabsorption calculations.[2,18] The present results and our recently published[19] data on alkali metal layers, indicate that the width of the multipole plasmon increases with increasing electron density. This trend agrees with the published theoretical results.[2,14] The multipole plasmon appears at a relative frequency of $\omega_m=0.85\omega_p$ with respect to the bulk plasmon frequency. It should be noted that the time-dependent local-density approximation (TDLDA) jellium calculation, which takes into account the exchange correlation potential, predicts this value to be $0.8\hbar\omega_p$.[14] The appearance of the multipole at somewhat higher frequency compared to the calculation indicates that the electron density is possibly less polarizable on the Al(111) surface as compared to a jellium surface.[1] It is interesting to note that the multipole plasmon appears at a similar relative frequency (around $0.8\omega_p$) for all metals so far studied irrespective of their electron density.[1,19] Although the different theoretical calculations agree on this aspect, the physical reason for this behavior is not fully understood.[1] In the work by Levinson, Plummer, and Feibelman on Al(100),[9] the multipole plasmon peak appears around 12.5 eV ($0.83\omega_p$) and the overall shape of the peak is similar to the Al(111) surface. However, taking advantage of the high quality of data it would be interesting to investigate the crystal face dependence of photoyield. A significant increase of intensity is observed in the experimental spectrum below 7 eV, towards the work function cutoff. This is the evidence for the collective threshold excitation phenomenon which has been predicted by TDLDA calculations.[17]

We now turn to the discussion of the photoyield in the region above the multipole plasmon response. The spectrum in the frequency region above ω_p shows two weak humps around 20.5 (feature A) and 16 (feature B) eV (shown by arrows in Fig. 1). The occurrence of these features is surprising, since according to LDA-based jellium calculations, the total photoabsorption above ω_p is featureless.[15] Data on Al(100) by Levinson, Plummer, and Feibelman also exhibit a broad feature around 20 eV.[9] These features are not due to a larger photoemission matrix element for certain final states, to which the states at E_F can couple (as in the final state resonances), since they remain at the same energy position for different initial states (between 0 to 1 eV binding energy). Moreover, the shape of the final bands is such that there are no direct transitions from the Fermi level in this photon energy. In order to understand the origin of these features, AERPY spectra (open circles) have been recorded as a function of angle of incidence (α) ($20°\leqslant\alpha\leqslant55°$) for normal emission collection geometry (Fig. 2). It turns out that the higher energy feature A shifts systematically to lower energies with decreasing α, while feature B does not shift. As indicated by arrows, at $\alpha=55°$ feature A is around 23 eV and moves to 20.3 (19.2) eV at $\alpha=45°$ (40°). At $\alpha=35°$ it appears around 18 eV and overlaps with feature B. At $\alpha=25°$ the two features completely overlap, resulting in an enhanced and broadened peak, while at $\alpha=20°$ this peak becomes narrower. In contrast, the multipole plasmon at 13 eV does not shift with angle, its origin being due to nonlocal effects that cannot be explained by Fresnel theory. The shoulder appearing at 10.6 eV in this set of AERPY spectra is due to the excitation of the monopole surface plasmon that appears at $\hbar\omega_p/\sqrt{2}$ (10.6 eV). A relatively rough surface can provide the momentum for the monopole surface plasmons to be excited by the photons. The surface plasmon, which has been seen in earlier photoyield studies,[4–6,9] does not appear in the data shown in Fig. 1 where a different crystal with a carefully electropolished surface was used. The weak glitch at 24 eV (Fig. 2) is related to the Al $2p$ core-level intensity, excited by the third-order light from the toroidal grating monochromator, moving through E_F.

In order to understand the changes in the AERPY spectra above $\hbar\omega_p$, we have calculated the electric field within the surface, using the classical Fresnel equations for *p*-polarized light.[25] The experimentally determined refractive index (n) and the extinction coefficient (k) (Refs. 26, and 27) for Al (shown in Fig. 3) were used as inputs to the calculation. The geometry of the experiment is such that the plane of inci-

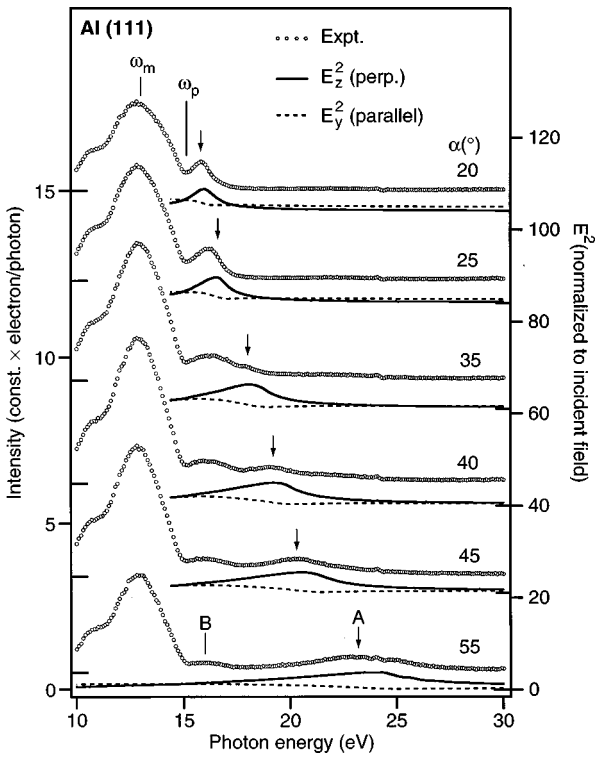

FIG. 2. Angle- and energy-resolved photoyield spectra of Al(111) measured at normal emission collection geometry with *p*-polarized light as a function of the angle of incidence (α). The spectra are shifted with respect to each other, and the zero of each spectrum is indicated on the left vertical axis. E_z^2 (solid line) and E_y^2 (dashed line) are the calculated perpendicular and parallel components of the Fresnel fields inside the surface, normalized to the incident field. The calculated curves are shifted with respect to the experimental spectra for ease of comparison, and the zero is shown on the right vertical axis. The arrows show the dispersion of feature A.

dence is a mirror symmetry plane of the crystal; for normal emission, the final state is symmetric. Thus, considering the symmetry (Λ_1) of the initial state at E_F, photoelectrons from the Al(111) surface are excited only by the normal (E_Z) component of the *p*-polarized light. Figure 2 shows the calculated E_z^2 (normal) and E_y^2 (parallel) components of the electric field as functions of photon energy for different α.

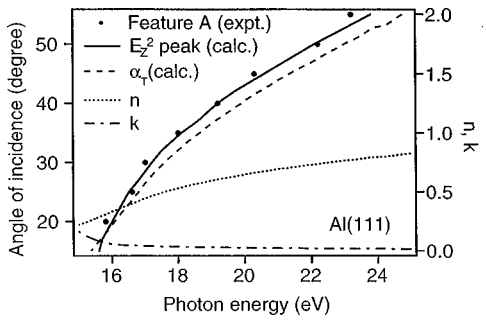

FIG. 3. Comparison of the energy position of feature A (filled circle) with the peak position of calculated E_z^2 (solid line) and the angle of incidence for the onset of total internal reflection $\alpha_T(h\nu)$ (dashed line). Refractive index (n) and extinction coefficient (k) of Al refer to the right vertical axis.

E_z^2 ($h\nu$) exhibits a broad peak for $\alpha=55°$, which becomes narrower and shifts systematically to lower energies with decreasing α. The E_y^2 component exhibits a steplike feature at the same frequency where E_z^2 exhibits a peak, and has no counterpart in the experimental spectra. In Fig. 3 we compare the position of feature A with that of E_z^2 and the agreement is found to be excellent. The intensity measured in the AERPY spectrum is due to photoemission from states at E_F, which is governed by the photoemission matrix element, $|\langle f|\mathbf{A}\cdot\mathrm{p}+\mathbf{p}\cdot\mathbf{A}|i\rangle|^2$, where $\mathbf{A}$ is the vector potential, $\mathbf{p}$ is the electron momentum, and $|i\rangle$ and $|f\rangle$ are the initial and final states, respectively. On increase of the electric field (E_Z) within the surface, the matrix element and hence the photoyield is enhanced. For this reason, the dispersion of feature A and the peak of the normal component of the Fresnel field are in good agreement (Fig. 3), signaling the success of Fresnel theory to explain this single-particle excitation related feature. A dip at 15 eV appears in all the spectra because at $\hbar\omega_P$ ($\approx$15 eV for Al) the surface becomes transparent to the incident photons. The total photoabsorption at $\hbar\omega_p$, according to the theoretical formulations,[2] is zero. However, the experimental spectrum shows a finite intensity at the dip which increases for decreasing α due to the dispersion of feature A towards lower energy. Thus, the finite intensity at the dip occurs in part due to photoemission from within the surface, and the disagreement with theory arises because only surface photoabsorption is considered in the formulation.

The calculated angle of incidence for the onset of total internal reflection, $\alpha_T[=\sin^{-1}(n)]$, is shown as a function of photon energy in Fig. 3. For example, at $\alpha=30$, total internal reflection occurs for $\hbar\omega\leqslant 17.6$ eV. The extinction coefficient (k) is small compared to the refractive index (n) in the energy range of interest (Fig. 3). In such a situation, the maximum of E_Z^2 as function of α occurs around α_T. The variation of n and k with photon energy shifts this maximum as well as α_T in a similar way. Thus, the variation of the maximum of $E_z^2(\hbar\omega)$ with α, exhibits a similar variation as that of α_T as a function of photon energy (Fig. 3). So, the dispersion of feature A is correlated to $\alpha_T(\hbar\omega)$. An important outcome of this observation is that, for surfaces with an unknown refractive index, photoyield data could be used to obtain such information. The shape of the E_z^2 peak is similar to that of feature A, which could also be used to extract the $\hbar\omega$ dependence of the optical constant; however, a possible variation of the photoemission matrix element needs to be considered. Moreover, the presence of direct transitions, final state resonances, or collective excitations would complicate the analysis.

Feature B, which appears at $1.07\hbar\omega_p$ (16 eV), does not disperse with angle, unlike feature A. The behavior is similar to features related to collective excitations (viz, the multipole plasmon) that do not disperse. E_z^2 does not show any enhancement in that region (Fig. 2), which means that feature B cannot be explained by classical Fresnel fields. The total photoabsorption calculations by Feibelman using the LDA-based random phase approximation technique[2] indeed show a hump between ω_p and $1.2\omega_p$. This feature is observed only when the microscopic variation of the field is taken into account, as in the case of the multipole plasmon,[9] indicating

that the origin of feature B is related to a collective excitation. We have found a similar feature for thick K layers grown on Al(111).[19,28] The spectra exhibits a dip at 3.8 eV ($\hbar\omega_p = 3.8$ eV for K) with a feature appearing at 4 eV, which is at a similar relative frequency of $1.05\omega_p$, as in Al. When an electromagnetic wave with $\omega \geqslant \omega_p$ is incident, longitudinal electrostatic waves associated with oscillatory charge densities exist in a conducting medium along with the transverse electromagnetic field. For *p*-polarized light, the longitudinal and transverse waves can interfere at the surface.[1] The excitation of bulk plasmons ($\omega \geqslant \omega_p$) at the surface or in thin films of a conducting medium have been related to the longitudinal polarization wave.[29] Thus, the peak ovserved at 16 eV finds a natural explanation in terms of photon induced excitation of longitudinal bulk plasmons with $q > 0$. To our knowledge, this is the first experimental observation of such a coupling in a metal surface. Detailed calculations might provide an explanation for the shape of this feature as a function of frequency.

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