Bulk and surface plasmon excitation in the interaction of He\(^+\) with Mg surfaces

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Abstract

We report on studies of plasmon excitation in Mg under the impact of slow He\(^+\) ions in the incident energy range 0.1–0.5 keV. Consistent with studies on Al surfaces, a transition from surface to bulk plasmon excitation occurs as the energy of the ion is increased. Previous methods in the literature to obtain information about yields of electron emission from plasmon decay are discussed. A new data analysis procedure is presented, which allows disentangling the contributions to the experimental spectra arising from different emission mechanisms, showing that potential excitation of multipole surface plasmons gives an important contribution to electron emission.

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1. Introduction

Neutralization by electron capture of slow ions at metal surfaces releases potential energy that can excite plasmons [1], quantized collective oscillations of the metal charge density. Plasmons of energy \(E_{pl}\) can be excited if \(E_n \approx E_{pl}\), where \(E_n\) is the potential energy transferred to the solid. The excited plasmons then decay by excitation of valence electrons resulting in electron emission, which is experimentally identified by a characteristic structure produced in the energy distribution of emitted electrons. This structure shows a high-energy edge at \(E_m = E_{pl} - \Phi\) [1,2], where \(\Phi\) is the metal work function, corresponding to the emission of an electron from the Fermi level.

Plasmon excitation and decay competes with the well-known mechanisms for potential electron emission at metal surfaces [3,4]: Auger neutralization, that involves two electrons from the solid, and resonant neutralization followed by interatomic Auger deexcitation. Since the work by Baragiola and Dukes [5], suggesting that electron emission from plasmon decay is more important than Auger neutralization, several investigation [6–12] have been performed to study potential electron emission from free electron metals, but the question of the competition between plasmon excitation and Auger processes has not yet been answered.

Most of the studies of potential plasmon excitation have considered ion impact on Al surfaces.
The difficulty in experiments on Al samples is the strong overlap in the plasmon and Auger structures in the electron energy spectra. The Auger neutralization structure has a maximum energy at $E_b = I' - 2\Phi$, where $I'$ is the ionization potential of the parent atom shifted by the image interaction. This structure is thus separated in energy from the plasmon by $I_0 / C_0 U$. Furthermore, the distinction between the two structures can be done by observing the different behavior of the broadening of the Auger and the plasmon structure with changes in the ion velocity [7]. In Al, the two structures can be distinguished only in the case of incident He$^+$ ions [5,10], while for Ar$^+$ ions no plasmon structure is observed [7], and for Ne$^+$ no clear Auger structure has been resolved [5,7,8].

In contrast, the spectra of electron emission from Mg surfaces by slow ions carrying high potential energy, such as He$^+$ and Ne$^+$, show that the plasmon decay and the Auger structures are clearly separated in energy [1], due to the lower energy of the plasmons of Mg.

Experiments on Mg surfaces appear, then, to be better suited to study the role of plasmon decay in potential electron emission. To this end, we measured energy distribution of electrons emitted from Mg surfaces under the impact of slow He$^+$ ions. Consistent with previous research [7,8], the plasmon structure observed in the spectra induced by slow He$^+$ ions is attributed to decay of multipole surface plasmons [9] excited by the potential energy released by the neutralization at the surface of incoming ions. Bulk plasmon excitation appears at our highest impact energies.

We discuss methods to extract yields of electrons from plasmon decay from the experimental spectra. A very simple data analysis procedure allows disentangling the contribution given by multipole plasmon decay from that by Auger processes and from a low energy peak due to electronic collision cascade.

2. Experiments

The experiments were performed in an ultra high vacuum (base pressure $\sim 1 \times 10^{-10}$ Torr) surface science system used in previous electron emission studies [5], using a double-pass, cylindrical mirror, electron energy spectrometer. The spectrometer was operated at constant pass energy of 50 eV and a resolution of 0.2 eV. The energy scale was calibrated to refer to the vacuum level of the Mg sample [5]. The surface of the sample was normal to the axis of the spectrometer and at $12^\circ$ with respect to the ion beam direction. Ions were produced in an electron impact source, which was operated at an electron energy of 58 eV. The polycrystalline Mg surface was sputter cleaned by 4 keV Ar$^+$ ion bombardment and cleaning was monitored by ion and electron induced Auger electron spectroscopy.

3. Results

In the upper panel of Fig. 1, we report energy distributions $N(E)$ of electrons emitted by the Mg surface under the impact of 160–460 eV He$^+$ ions. The spectra in Fig. 1 have been normalized so that their area equals the electron emission yield $\gamma_{tot}$ as in [5], being consistent with those previous studies. They show two structures labeled $a$ and $b$, superimposed on a background peak of cascade electrons [4]. These structures appear clearer in the derivative of the spectra shown in the lower panel of Fig. 1.

The energy of the structure $b$ is consistent with the energy $E_b = I' - 2\Phi$ ($\Phi = 3.75$ eV is the work function for polycrystalline Mg) expected for the high-energy edge of the spectrum of the electrons emitted from the Mg surface by Auger neutralization. This attribution is confirmed by the observed broadening of the electron energy distributions $N(E)$ with increasing projectile energy (see inset in Fig. 1). This broadening is typical of neutralization via Auger processes and results from the atomic energy level shift near the surface and incomplete adiabaticity due to ion motion normal to the surface [13]. Furthermore, the spectra shown in Fig. 1 intersect at a “magical” point [14], another characteristic of velocity broadened Auger spectra, which corresponds to the minimum of the structure $b$ observed in the derivative.
The structure labeled \(a\) does not depend on the ionization potential of the incoming ions [5]. Consistent with studies [7,8] on Al surfaces, structure \(a\) is assigned to electron emission from decay of multipole surface plasmons, while bulk plasmon excitation appears at higher impact energy as shown in Fig. 2.

The transition from multipole to bulk plasmon excitation is shown in Fig. 2 Panels (a)–(d) of Fig. 2 report the plasmon dips observed in the derivative of the spectra revealed at growing incident ion energies. At 260 eV incident energy, the plasmon shoulder results in a minimum in the derivative at \(E_m \sim 6.2\) eV, i.e. 0.9 eV less than the energy of the \(q = 0\) bulk plasmon structure appearing in the electron excited spectrum [1]. This energy value is consistent with the attribution to electron emission from decay of multipole surface plasmons excited at or above the surface by potential energy transfer upon neutralization of incoming ions.

At an incident energy of 4.5 keV, the plasmon structure appears at an energy that is consistent with that of the Mg bulk plasmon. The spectra acquired at intermediate energies show the transition...
from surface to bulk plasmon excitation. As the energy of the incident ion is increased, we notice in Fig. 2 that the structure due to bulk plasmon decay grows on the high-energy side of the surface plasmon decay structure.

4. Discussion

The task of obtaining information about the electron yields for plasmon decay is rather difficult due to the overlap of structures arising from several processes. Several procedures have been applied [15,16] to disentangle the plasmon structure from the background due to other electron emission phenomena. Fig. 2 illustrates the application of one this procedure [16], based on the analysis of the derivative of the spectra, to the case of electron emission by He$^+$ ion impact on Mg surfaces.

Panels (a)–(d) of Fig. 2 report examples of background subtraction from the derivative of the spectra. The background curve was obtained by fitting two regions on both side of the plasmon structure with a polynomial function. Panels (e)–(h) report the negative peaks obtained after the subtraction. We observe that at 460 eV incident energy the structure is well reproduced by a Gaussian curve centered at an energy below that corresponding to a bulk plasmon decay structure and assigned to decay of multipole surface plasmons. At higher incident energies, the structure is not reproduced by only one curve, but by the superposition of two Gaussians of constant width and position corresponding to the surface and the bulk plasmon features. The areas $A_{SP}$ and $A_{BP}$ of these Gaussians are shown as a function of incident energy in the upper panel of Fig. 3. Also shown in the lower panel of Fig. 3 is the ratio $R = A_{BP}/\gamma_{tot}$.

The analysis shown in Figs. 2 and 3 compares well with similar results obtained in the case of experiments of Ne$^+$ ion impact on Al surfaces [8], showing that the procedure gives valuable insight into the mechanisms for plasmon production in free electron metals by slow ions. In [16], it has been discussed that absolute electron yields from surface and bulk plasmon decay could be obtained by multiplying by a factor $C = 2E_F/3$ the areas of the corresponding Gaussians in Fig. 2. However, we find that this value of the factor $C$ is a good approximation only for very narrow plasmon width, while for plasmon structure whose width is about 2 eV, like in Mg and Al, this value is underestimated by about 40%. Furthermore, as will be shown later in this section, the particular choice of the background curve affects the areas of the plasmon structure in the derivative resulting in a further strong underestimation. Therefore, to study the relative contribution to electron emission from plasmon decay and neutralization via Auger
processes, we adopted the procedure shown in Fig. 3.

The energy distribution \( N(E) \) of emitted electrons can be written as \( N(E) = T(E)N_0(E) \), where \( N_0(E) \) is the internal energy distribution, i.e. the spectrum of electrons excited in the solid at energy \( E \) above the vacuum level and \( T(E) \) is the surface transmission function, giving the probability for an electron of excitation energy \( E \) to be transmitted through the surface. As shown in Fig. 1, electron cascade, plasmon decay and Auger electrons contribute to \( N(E) \). Thus, we have \( N_0(E) = N_{0K}(E) + N_{0P}(E) + N_{0A}(E) \), where \( N_{0K}, N_{0P}, N_{0A} \) are the internal energy distribution of electrons excited respectively by the three processes. In the case of experiments on Mg samples, the three emission mechanisms are well separated in energy. Fig. 4 shows the attempt to reproduce the experimental spectrum \( N(E) \) of electrons emitted by 460 eV He\(^{+} \) ion impact by modeling the three internal distributions in the very simplest fashion and by using a suitable choice for \( T(E) \) as Eq. (16) in [4].

As in [16], for \( N_{0P} \) we considered the convolution of a parabolic density of states with a Lorentzian. We found that a width \( \Gamma_{pl} \sim 1.7 \) eV, which is consistent with the width of the plasmon structures we observed in electron energy loss experiments, yielded a good reproduction of the experimental spectrum. The other adjustable parameter in \( N_{0P} \) is \( E_m \), the high-energy edge of the plasmon decay structure. The value of \( E_m \) we found agrees with the expectation of multipole plasmon decay (the multipole plasmon energy is \( \sim 0.9E_{vp} \), where \( E_{vp} \) is the \( q = 0 \) bulk plasmon energy).

For \( N_{0A} \) we considered the self-convolution of a parabolic density of states to represent Auger transitions involving two electrons in the Mg conduction band and a hole in the incoming ion. A Lorentzian broadening of a \( \sim 0.5 \) eV was introduced in the convolution and the energy released in neutralization, \( E_n \), was varied to reproduce the position of the structure, thus taking into account the image energy shift. This simple model can reproduce the Auger structure well, except for the high-energy tail. However, this discrepancy does not introduce a significant error in the estimation of the area of the structure, and is therefore neglected here to keep the description on the simplest grounds.

For \( N_{0K}(E) \), we found that a simple exponential function of the type \( a^{-bE} \) yielded a good reproduction of the cascade peak. Fig. 4 shows that the experimental spectrum can be reproduced satisfactorily, allowing the estimation of the relative contribution to electron emission due to plasmon decay and Auger neutralization, i.e. the ratios \( R_{SP} = \gamma_{SP}/\gamma_{tot} \) and \( R_A = \gamma_A/\gamma_{tot} \), where \( \gamma_{SP} \) and \( \gamma_A \) are the electron yields for the two process respectively. We find \( R_{SP} = 0.25 \) and \( R_A = 0.15 \). The uncertainties in these values are estimated to be about 15% by varying the relative weight of the
three calculated energy distributions in the reproduction of the experimental spectrum and also by using other functional forms for \( N_{0k}(E) \), as well as for the surface transmission function \( T(E) \).

To further check the reliability of the analysis, the lower panel of Fig. 4 shows that the procedure gives also a good reproduction of the derivative of the experimental spectrum, where the plasmon feature is clearer. This observation confirms that the plasmon excitation is needed to explain the data and that its contribution to the electron emission spectrum is properly estimated.

It is interesting to notice that the background given by the derivative of the cascade peak is significantly different from that shown in Fig. 2. Subtraction of this background from the derivative of the experimental spectrum results in the negative peak shown in Fig. 5, which has an area about twice larger than the subtracted peak shown in panel (e) of Fig. 2. The subtracted structure in Fig. 4 shows the Lorentzian broadening due to finite plasmon lifetime, but it is also fairly well reproduced by a Gaussian distribution, thus justifying the use of Gaussian curves so far adopted in Fig. 2 and in the literature [8,16]. The different tailing of the two distributions is masked when the background shown in Fig. 2 is subtracted from the experimental data.

In conclusion, the results presented in this work are consistent with the physical picture depicted in previous studies of plasmon excitation in free electron metals by slow ions. Low momentum bulk plasmons are observed for incident energies in the kinetic electron emission regime [4], in which electron excitation is mostly determined by the transfer of the kinetic energy of the projectile.

At lower energies, where electron emission is mainly determined by the transfer of the potential energy released when incoming ions neutralize, we observe the excitation of multipole surface plasmons.

We have shown that existing methods of analysis of the derivatives of the experimental spectra give valuable insight into the mechanisms for plasmon excitation by slow ions, but require particular care in the attempt of extracting yields of electron emission from plasmon decay. Therefore, we applied a different procedure based on the analysis of the spectra.

Our admittedly simplified data analysis cannot fully account for the wealth of information contained in the spectra, which call for theoretical investigation. Nevertheless, it strongly supports the important conclusion that electron emission from plasmon decay is more intense than that from Auger neutralization. This result is in contrast with recent works [10–12], where plasmon excitation and decay was discussed as a minor contribution to potential electron emission from Al surfaces under ion irradiation [10–12], and confirms the importance of potential plasmon excitation in ion neutralization at free electron metal surfaces.

References