Plasmon Excitation by Multiply Charged Ne^{q+} Ions Interacting with an Al Surface

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The emission of low-energy electrons caused by 4.5 keV Ne^{q+} ion impact on an Al surface was measured for incident charge states $q = 1-6$. The electron spectra exhibit structures near 6.5 and 11 eV which are attributed to the creation of surface and bulk plasmons, respectively. The signature for bulk plasmon disappears for $q = 6$. It is argued that, for the higher charge states, the bulk plasmons are selectively created below the surface where the resonance condition for plasmon-assisted electron capture is achieved. [S0031-9007(98)05706-8]

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Collective phenomena of electron excitation in metals by charged particles have attracted considerable attention as these phenomena provide important information about fundamental solid-state properties. It is well established that conduction band electrons in metals can take part in collective oscillations of frequency ω_p known as plasmon oscillations. The production of plasmons by charged particles can be described within the framework of the free-electron gas approximation, where the electrons are assumed to move independently of the ionic potentials of the lattice atoms [1,2]. To derive specific plasmon properties, the random phase approximation (RPA) is generally used [2,3].

For nearly-free electron metals (e.g., Al), the decay of a plasmon produces an electron-hole pair by interband transitions leading to the transfer of an electron into the continuum. In the case where a plasmon transfers its energy to an electron at the Fermi level, the energy of the ejected electron is equal to $\hbar\omega_p - \phi$, where ϕ is the work function of the metal [4,5]. Hence, electrons of characteristic energies are ejected from the metal providing a signature for plasmons which can experimentally be studied using the method of electron spectroscopy.

Previous experiments have revealed clear evidence for plasmon excitation in the bulk as well as at the surface [6]. Most of the experiments have been performed using electron impact (see, e.g., [7–9]), whereas the number of ion impact studies is still relatively small [10–12]. Benazeth *et al.* [10] and Hasselkamp *et al.* [11] have used fast projectiles to create plasmons via direct Coulomb excitation which is constrained by momentum and energy conservation. Within the framework of the RPA, the ion velocity must exceed a lower limit which corresponds to an energy of about 40 keV/u for Al [13].

Mechanisms different from direct Coulomb excitation are expected when slow heavy ions are used in the experiment. Baragiola and Dukes [14] found evidence for plasmon excitation in emission spectra produced by Ne^+ and Ar^+ with energies as low as 50 eV. These low-energy projectiles were incident at grazing angle, and they are not expected to penetrate into the solid. However, structures in the electron emission spectra were observed at an energy characteristic for bulk plasmons. To explain their observation, Baragiola and Dukes [14] considered a plasmon-assisted neutralization process, where potential energy of the projectile liberated in the capture process is used for plasmon creation. Similarly, Monreal [15] studied such a neutralization process, but attributed the structures observed for Ne^+ impact to surface plasmons whose energy is shifted.

Plasmon creation may be enhanced by multiply charged ions since their potential energy becomes significant. The large potential energy of highly charged ions has attracted much interest in studies of ion-solid interactions, see [16] and references therein. Above the surface, highly charged ions strongly attract several electrons which are resonantly captured into high Rydberg states, whereas inner shells remain empty. Thus, the projectiles evolve into hollow atoms whose formation and decay imply various novel processes.

As the hollow atom enters into the solid, the Rydberg electrons are removed while dynamic screening effects produce a strong cloud of conduction band electrons around the projectile. This cloud leaves inner shells empty so that a compact hollow atom is formed below the surface. When the hollow atom moves within the solid, its potential energy is transferred to the solid via Auger transitions and collisional charge transfer [17]. Hence, we expect that hollow atoms may also play an important role in the creation of plasmons. To our knowledge, no experimental results have been reported for plasmon excitation by slow highly charged ions, however. We should mention that the low-energy electrons produced by plasmon decay are difficult to measure since various instrumental effects may produce uncertainties in the experimental data.

In this paper, we study plasmon creation by the impact of 4.5 keV Ne^{q+} with charge states from $q = 1-6$ on a clean Al surface. Particular effort was devoted to achieve reliable electron yield measurements in the low-energy range where the signatures for plasmons occur. Structures found near 6.5 eV are attributed to the production of surface plasmons. Moreover, the electron spectra indicate structures

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near 11 eV associated with bulk plasmons which remain significant for charge states as large as $q = 5$. To explain these results, we consider a scenario for the potential-energy transfer which involves a selective creation of bulk plasmons at a few atomic layers below the surface.

The experiments were carried out at the 14.5 GHz electron cyclotron resonance source at the Ionenstrahl-Labor in Berlin using the ultrahigh vacuum chamber described previously in detail [18,19]. Beams of 4.5 keV Ne^{q+} ($q = 1-6$) ions were collimated to a diameter of about 1 mm and directed on a clean Al target. The emission of electrons from the target was measured using an electrostatic parallel-plate spectrometer [20]. In the target chamber, a pressure of a few 10^{-10} mbar was maintained. To measure absolute values for electron emission, the spectrometer efficiency and the ion current were determined. Auxiliary measurements were performed by means of 1 keV electron impact as a benchmark on the procedure.

The experimental setup was optimized to measure accurately low-energy electrons. A μ-metal shield inside the scattering chamber reduces the magnetic field to a few milligauss in the neighborhood of the spectrometer. The target and spectrometer surfaces were carefully cleaned to reduce perturbing electric fields due to charge buildup. Our experience shows that the spectrometer is capable of measuring reliable electron yields for energies as low as 2 eV. More information is given in Ref. [19].

Figure 1 shows experimental results for the double differential electron emission yield $N(E) = d^2\mathcal{N}/d\Omega\, dE$ at an angle of incidence of $\psi = 45°$ and an observation angle of $\alpha = 15°$ relative to the target surface. The uncertainties of absolute electron yields are $\pm 30\%$, and the relative uncertainties are $\pm 20\%$ with respect to a variation of the incident charge state. The electron spectrum for each charge state exhibits a maximum at low energies. The electron cascade maximum [21] is expected at about 2 eV and, indeed, observed for Ne^+ (Fig. 1). However, the low-energy maximum is observed to shift upwards in energy as the charge state increases reaching a value of about 4 eV for $q = 6$. A detailed study of this remarkable energy shift lies outside the main scope of the present paper, and it is only noted here that the present finding is consistent with previous observations for highly charged ions [22,23].

A significant feature of the spectra in Fig. 1 is the increase of the electron yield with increasing charge state. It is expected that, for Ne^{q+} incident with $q = 1$, the electrons are ejected primarily by means of kinetic electron emission, where the projectile transfers energy in collisions with the target electrons [14]. The increase of the electron intensity with increasing charge state is due to the onset of potential electron emission [24] which is found to be roughly proportional to the corresponding potential energy. As shown previously [19], the electron emission is caused primarily by dielectronic processes above and below the surface. Above the surface, autoionizing transitions in higher Rydberg states give rise to electron energies as low as a few eV, whereas the L-Auger electrons originate primarily from below the surface.

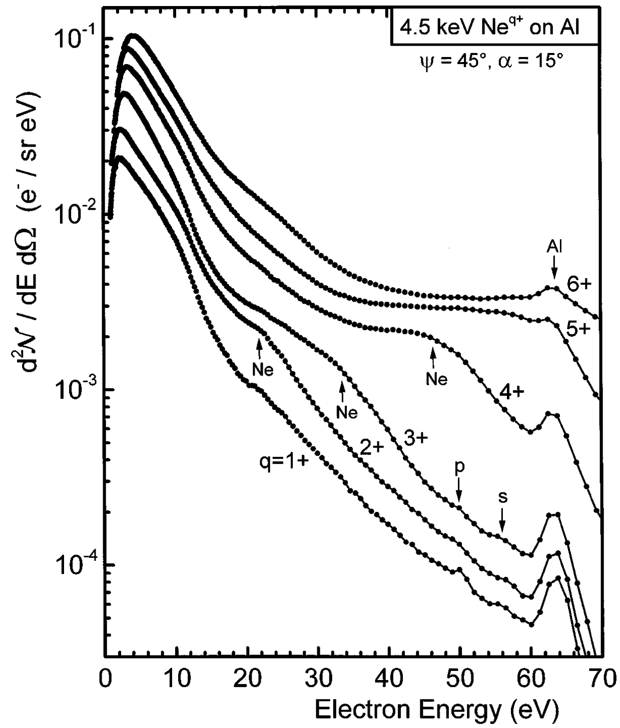

FIG. 1. Double differential emission yields $d^2\mathcal{N}/dE\, d\Omega$ for electrons produced by 4.5 keV Ne^{q+} incident on an Al surface for $q = 1-6$. The maxima labeled Al and Ne are due to L-Auger electrons from the Al target and the Ne projectile, respectively. The small structures labeled p and s are tentatively attributed to Al L-Auger electrons which have lost discrete energies by plasmon excitation in the bulk and surface, respectively.

For instance, L-Auger transitions in the Al lattice atoms give rise to a pronounced peak near 63 eV [10]. The vacancies in the Al L shell are produced in binary collisions with the hollow Ne projectile [17]. Moreover, L-Auger electrons from Ne^{q+} projectiles for $q = 2$, 3, and 4 are seen near 22, 34, and 46 eV, respectively. The increase of the L-Auger energy with charge state may be understood from Table I, which shows that the energy liberated by electron transitions into the Ne L shell becomes larger as the number of Ne $2p$ vacancies increases. These energies were calculated using the density-functional theory for hollow Ne atoms decaying inside the solid [25].

To enhance the visibility of the structures due to plasmon decay, which are superimposed on an intense background from other processes, it is common practice to differentiate the measured electron intensities $N(E)$ [2]. Before evaluating the derivative dN/dE, however, we applied a Fourier transformation smoothing procedure which has no significant effect on the energy resolution. The results are presented in Fig. 2. Note that the derivative dN/dE increases with charge state similarly as the original spectra in Fig. 1.

TABLE I. Electronic transition energy from the bottom of the conduction band of Al to the $2p$ level of a hollow Ne atom which contains a number of $2p$ vacancies. The results are based on total energies evaluated using the density-functional theory [25].

Number of $2p$ vacancies	1	2	3	4	5	6
Transition energy (eV)	12.8	23.6	33.4	45.6	56.7	68.8

First, we consider Fig. 2(a), which shows auxiliary data for a 1 keV electron impact which compare well with previous results [8]. The derivative dN/dE indicates a dip at 6.5 eV and at 11 eV which can be associated with the decay of surface and bulk plasmons, respectively. In Figs. 2(b)–2(f), the data for 4.5 keV Ne^{q+} impact with $q = 1$–4 and 6 are given. The curves show structures which can be associated with plasmon decay. For $q = 1$, the present data compare well with the previous results by Baragiola and Dukes [14]. The derivative dN/dE for $q = 1$ clearly shows a structure near 11 eV which is commonly attributed to bulk plasmons. This structure is enhanced for $q = 2$ but becomes less pronounced in comparison with the background as the charge state further increases to $q = 5$. Finally, the bulk plasmon structure seems to disappear for $q = 6$.

The derivative dN/dE shows an additional structure which is shifted from about 6 to 7.5 eV as the incident charge state increases from $q = 1$–6. Hence, this structure is close to 6.5 eV where the signature for surface plasmons occurs, see Fig. 2(a). The structure near 6.5 eV has not been previously observed with slow heavy ions. The spectral features at low energies could be viewed with some caution as they may be influenced by instrumental effects. Nevertheless, the present structure near 6.5 eV can be identified for all charge states including the highest value $q = 6$.

As a primary mechanism for plasmon production by slow heavy ions, we propose that the capture of a conduction band electron into the L shell of the Ne projectile provides the excess energy for plasmon creation. This plasmon-assisted capture process is similar to those considered by Baragiola and Dukes [14] and Monreal [15]. However, we note that, in our case, the projectile enters into the solid and the capture into the L shell occurs primarily below the surface. Moreover, the higher charge states of the projectile differentiate the present study from previous work.

Since the potential energy of the projectile increases with the charge state, at first it might be expected that the number of created plasmons also increases. Recall that the derivative dN/dE increases with the charge state (Fig. 2). However, the derivative shows that the intensity of the plasmon structures does not increase as strongly as the underlying intensity from dielectronic processes.

To explain this finding, we note that, due to energy conservation, the energy required for the plasmon creation must be close to the potential energy liberated by the projectile. The liberated energy is equal to the sum of the transition energy given in Table I (relative to the bottom of the conduction band) and the initial electronic energy above the bottom of the band. The latter value amounts to $\sim$5 eV if the captured electron originates from the screening cloud surrounding the hollow atom [25]. Bulk plasmon excitation requires 15–20 eV so an energy-matching (resonance) condition is fulfilled for Ne with a single vacancy in the $2p$ orbital (Table I). This is consistent with the finding in Fig. 2 that the bulk plasmon structure is significant for incident Ne^{+} (see also Ref. [14]). Similarly, for Ne^{2+}, plasmon production may still be resonant since the energy of the $2p$ orbital is reduced by promotion effects in the vicinity of a lattice atom [17]. Indeed, Fig. 2(b) shows that the bulk plasmon structure for $q = 2$ is also relatively large.

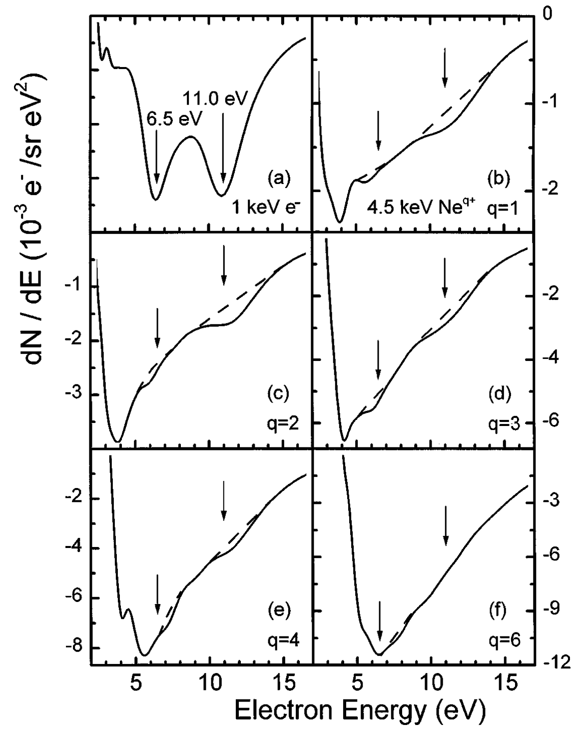

FIG. 2. Derivative dN/dE of the double differential emission yields given in Fig. 1. The results in (a) refer to 1 keV electron impact and those in (b)–(f) refer to 4.5 keV Ne^{q+} impact, where $q = 1$–4 and 6. The dips near 6.5 and 11 eV are attributed to surface and bulk plasmons, which were also observed for $q = 5$.

When more than two vacancies occur in the $2p$ orbital, it is unlikely that the resonance condition remains (Table I). However, for Ne^{q+} incident with $q > 2$, plasmons are still produced. This is due to the fact that the $2p$ orbital is successively filled in the solid [17]. At the end of the filling cascade when Ne projectiles with single or double $2p$ vacancies occur, resonance conditions may again be satisfied and plasmon-assisted capture may be possible. Nevertheless, we expect that the charge-state dependence of the plasmon intensity is weaker than that of the underlying background.

The important point of the present scenario is that plasmon production by a multiply charged projectile occurs a few atomic layers inside the solid. Consequently, the electrons induced by the plasmon decay may be attenuated when escaping from the solid. For example, using our previous cascade model for the filling of hollow atoms [17,26], we estimated that 4.5 keV Ne^{6+} incident at 45° reach a mean depth of 25 a.u. before the Ne $2p$ orbital is filled except for one remaining vacancy (resonance condition). The escape depth for 15 eV electrons is about 20 a.u. [27] so the emitted electron intensity is attenuated by a factor of ~ 3 as the electrons escape from the bulk. This attenuation is a significant reason for the disappearance of the bulk plasmon structure as the incident charge state increases to $q = 6$.

The mechanisms responsible for the production of surface plasmons are less well understood. Surface plasmons are likely to be produced when the ion approaches the solid or just touches the surface. Production of a surface plasmon requires 10.8 eV which may be provided by capture processes into higher lying shells. Above the surface, the projectile is less screened than in the solid and it has empty orbitals (e.g., $M, N, \dots$) which may provide the necessary energy independent of the charge state in a capture process. Thus, the nearly constant intensity observed for the surface plasmons might be understood. Furthermore, the shift of the surface plasmon structure is consistent with the evaluation by Monreal [15] mentioned above.

Apart from the capture process, other mechanisms for plasmon creation may be considered. Note that Ne orbitals higher than the $2p$ shell cannot participate in the bulk plasmon creation. The density-functional theory shows that no higher orbitals are bound within the solid [25]. However, energetic continuum electrons produced in collisions as well as Auger electrons may excite plasmons when traveling through the solid [13]. In fact, the latter process is indicated in the present spectra (Fig. 1) showing small structures at the low energy side of the Al-L Auger peak, which may be due to Auger electrons that have lost discrete energies by surface and bulk plasmon excitation. However, note that the corresponding intensities are relatively small so that they are not expected to contribute significantly to the plasmon production observed by electron emission (Fig. 2).

In summary, we observed clear evidence for plasmon excitation in electron emission spectra produced by slow multiply charged ions. Structures found near 6.5 eV are consistent with the creation of surface plasmons. Furthermore, the spectra exhibit structures at 11 eV due to bulk plasmons which are likely to be excited by the hollow atom reaching the final stage of its filling cascade. Thus, singly and doubly charged ions are expected to create bulk plasmons near the surface, in agreement with previous studies [14]. On the other hand, to achieve resonance conditions for highly charged ions, the projectiles must penetrate a few atomic layers into the solid. This requirement would offer the possibility to create plasmons at a selected depth depending on the charge state, the velocity, and the angle of the incident projectile. We plan further experiments to support the proposed scenario of highly charged ions producing plasmons.

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