Surface-topography dependence of line shapes in electron spectra due to decay of autoionizing states produced in inelastic ion-surface collisions

V. A. Esaulov,[1,*] L. Guillemot,[1] O. Grizzi,[2] and E. A. Sánchez[2]

[1]*Laboratoire des Collisions Atomiques et Moléculaires, Unité Mixte de Recherche UMR 8625, Bâtiment 351, Université de Paris Sud, Orsay 91405, France*

[2]*Centro Atómico Bariloche, Instituto Balseiro, CNEA, and CONICET, 8400 San Carlos de Bariloche, Río Negro, Argentina*

The line shapes of peaks in electron spectra due to decay of autoionizing states of Ne, formed in collisions of Ne with Al solid targets, were studied as a function of surface roughness. Strong variations in these line shapes were observed. These were modeled by taking into account the level shifts of the excited and ionic states of the atom in front of the surface and various resonant and Auger capture and loss processes. It is shown that rather complex line shapes may be expected. The electron spectrum generally possesses a peak at energies in the vicinity of that corresponding to autoionization of a free atom, as well as a high-energy tail and a secondary maximum. The intensity of the secondary maximum depends on how close to the surface most excited atoms decay and hence depends on surface flatness.

I. INTRODUCTION

A number of recent studies [1–6] have focused on the production of doubly excited autoionizing states of inert-gas atoms in collisions with metal targets. These states are a signature of inelastic, violent "binary" collisions of incident and target atoms. The study of their formation is interesting from the point of view of the study both of mechanisms of excitation and of various electron-transfer processes that are involved in their production. Experimentally these states are observed as well-defined structures or peaks in the electron spectra, which are superposed on a continuous background due to potential and kinetic electron emission. The electron energies at which they appear are found to be close to the ones expected for decay of these states for free atoms [7]. Shifts from these positions have been attributed to kinematic effects [1–5], i.e., due to emission from a moving source: a scattered atom, rapidly receding from the surface. Rather strong variations in the line shapes of these peaks have been observed, when the collision energy and especially the observation angle is varied [2]. Thus these peaks are generally asymmetric, with low- or high-energy tails, depending upon whether the observation angle, as measured with respect to the incident-ion-beam direction, is small or large, respectively. This behavior has been related to the characteristics of the ion angular distributions [2], which extend to rather large scattering angles and are characterized by large energy losses. Calculations [2] of the line shapes, assuming a δ-function *natural* line shape and taking into account kinematic and apparatus broadening effects, have been found to qualitatively reproduce some of these features.

Some indications about the natural line shapes are now available. It is now well known that in doubly charged ion scattering [8,9] on metals, electron spectra display broad peaks due to autoionizing states, which in this case are

formed on the *ingoing* trajectory and result from successive capture and loss processes, *before* the ion reaches the surface. The energy position of these peaks is not the same as in the scattered-ion case but is higher, due to shifts of the atomic levels near the surface. This shift also explains their large widths. Some model calculations of the line shapes of peaks resulting from autoionization of scattered particles moving away from the surface have been made, but no experimental data were available to compare with these predictions. In a recent study [10] we noted that the shapes of the peaks due to decay of autoionizing states vary quite strongly as a function of surface roughness, an effect that was tentatively ascribed to varying distances of decay from the surface, in relation to the above-mentioned simulation work [8,9]. Effects of roughness were also noted in the past in the polar angular distribution of secondary electrons emitted in Ar-Al collisions [11]. In this paper we present some data on the shapes of peaks in electron spectra due to decay of scattered excited Ne** atoms on surfaces of varying degrees of roughness, which are compared to the simulated spectra and found to be in quite good agreement, assuming that on rough surfaces decay of autoionizing states occurs further from the surface than on flat surfaces.

II. EXPERIMENTAL DETAILS

The experiments were conducted in an ultrahigh-vacuum chamber working at 3×10^{-10} Torr (with the beamline on). The ions were generated in a radio frequency source, mass selected, and collimated to better than 0.1°. The emitted electrons were analyzed with a custom-made [12] cylindrical-mirror analyzer working at 1% energy resolution and ±1° angular resolution. The inner cylinder of the analyzer rotates around its main axis, allowing measurements in a wide range of observation angles [12]. For the present measurements the incident direction was selected randomly and the observation angle fixed at $(\theta, \phi) = (21°, 5°)$, with θ measured from the ion-beam direction and ϕ from the scattering plane (inset of Fig. 1).

The preparation of the Al(111) sample was performed by

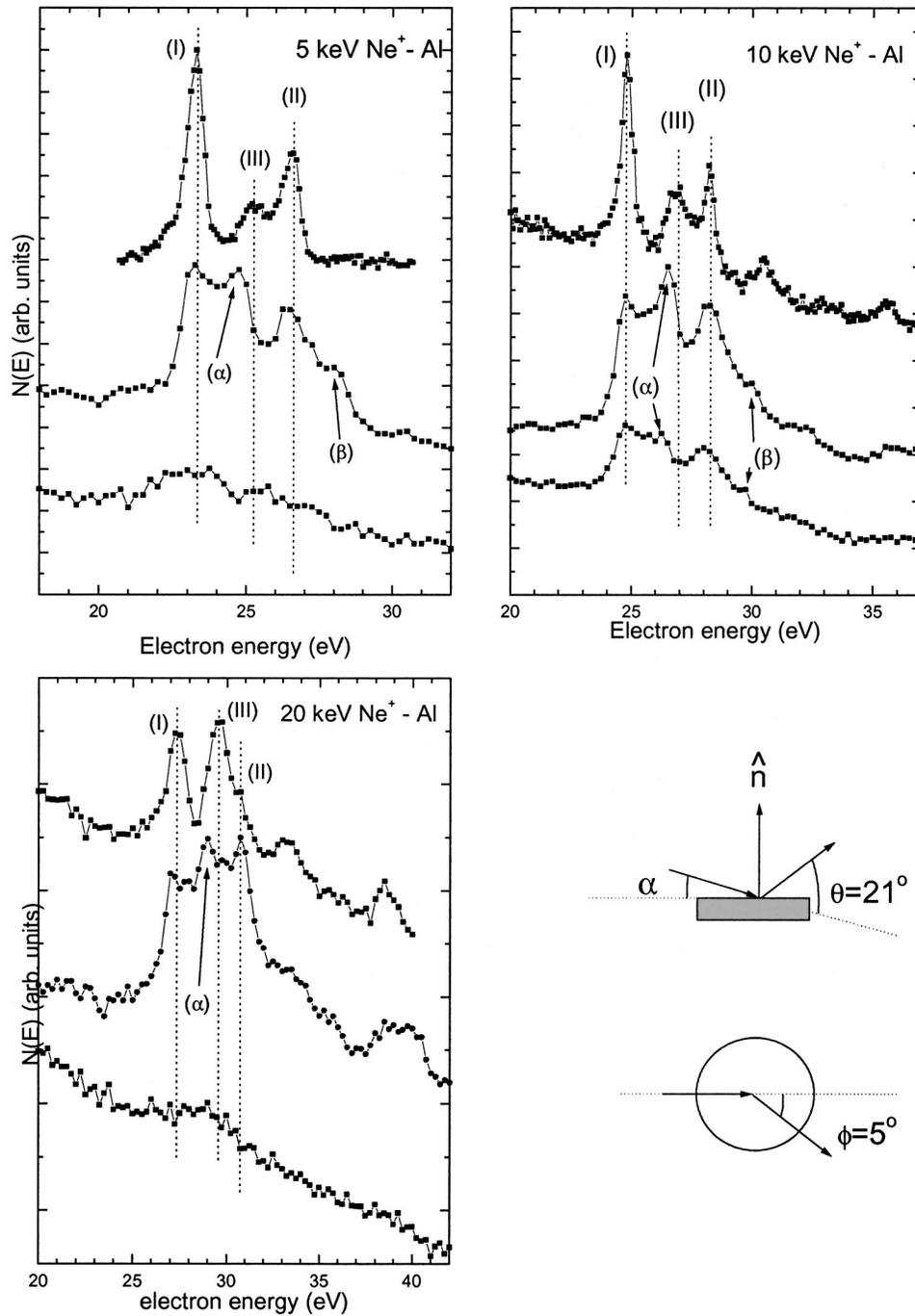*Corresponding author. Electronic address: esaulov@veof1.lcam.u-psud.fr

FIG. 1. Electron energy spectra in the region of the Ne** autoionizing state excitation for 5, 10, and 20 keV ion impact for an Al(111) surface with different degrees of roughness and a sketch of the scattering configuration.

repeated cycles of 20-keV grazing Ar bombardment and annealing at 450 °C. The azimuthal orientation of the surface was continuously changed during the Ar bombardment. As a result of these cleaning and polishing cycles, the surface presents long and flat terraces (at least 100 Å long) [13]. The cleaning of the surface was verified with Auger-electron spectroscopy before and after performing the measurements.

III. RESULTS

Figure 1 shows spectra in the region of the peaks due to decay of Ne** autoionizing states for 5, 10, and 20 keV ion impact for an Al(111) surface with different degrees of roughness. The spectra were all measured at low incident angles (between 3° and 6°). In all cases, the lowest spectra correspond to the flattest surface, i.e., one that was obtained immediately after the polishing cycles. For this surface the autoionizing lines are relatively weak and broad [10]. Increasing the surface roughness by means of large-angle (5°–10°) Ar or Ne bombardment results in a general enhancement of the Ne autoionizing line intensity and in a change in the line shape (middle spectra in Fig. 1). In particular, the main Ne autoionizing lines become structured with sharp peaks. As far as we known no previous report of this structured line shape has been given. For comparison, we also show in Fig. 1 spectra taken with a much rougher surface (top spectra).

These spectra from the very rough surface show sharp and well-defined features that are similar to those usually reported in past work [1–6]. The peaks I and II correspond to Ne** $(^3P)3s^2$ and $(^1D)3s^2$ states, which have been extensively investigated earlier. Note that these lines are shifted to higher energies because of kinematic (Doppler) effects, mentioned in the Introduction, and their positions change with projectile energy. In the projectile frame of reference the peak due to the decay of the Ne** $(^3P)3s^2$ state would be at 20.35 eV and that due to the $(^1D)3s^2$ state at 23.55 eV. Peak III, which becomes stronger at higher energies, presumably corresponds to a $2s2p^5nl$ state as discussed by us previously [10,14]. Its intensity, as well as that of other secondary lines, is enhanced by the grazing scattering geometry and the relatively large projectile incident energies [10].

In the case of the smoother surfaces the structure labeled α (appearing at energies 1.6–2 eV higher than peak I) cannot be interpreted in terms of the secondary line III. Note that it appears shifted in energy and has a different intensity from the structure observed for the rough surface. The shoulder labeled β, which appears at approximately the same distance from peak II, is present only for the smoother surfaces. The reasons for this behavior can be understood in terms of a model of formation of these states near the surface as a result of a series of electron-capture processes involving positive ions and deexcitation processes as the excited atom moves away from the surface. This model has been described in detail earlier [8,9,15]. In the following we shall briefly summarize some points of this model for clarity and compare its predictions with our data.

IV. THE MODEL

The doubly excited Ne** atoms are formed as a result of a violent, small-impact-parameter collision of an incident Ne ion or atom with a surface atom (see, e.g., [14]). On the basis of general considerations regarding excited-state formation in gas-phase collisions, it is expected that at low keV energies this binary collision will lead to the dominant formation of states of the $2p^4(^1D)$ Ne^{2+} core configuration. The exact nature of the excited species formed in this collision is not known. Very close to the surface, the energy levels of most excited states will lie above the Fermi level and are hence resonantly ionized, losing electrons to the conduction band. As the excited particle (excited atom or singly or doubly charged ion) leaves the surface, we have to consider a series of Auger and resonant decay and capture processes, which may lead to the experimentally observed final state distribution of Ne^{2+}, Ne^{+*}, Ne*, Ne$^+$, and Ne.

Here we adopt a simplified reaction scheme (see [15] for details) involving a series of electron capture and loss processes schematized in Fig. 2. The actual manifold of levels is replaced by the lowest terms and here we shall consider only the Ne^{+*} $2p^4(^3P)3s/3p$ and Ne** $2p^4(^3P)3s^2/3p^2$ excited states, in order to illustrate different cases of line profiles. Fine-structure splittings are neglected.

We assume that the excited species start out at a distance of the order of 2.5 a.u. from the image plane and consider their ejection into a range of θ_{ex}, with E_{ex} corresponding to
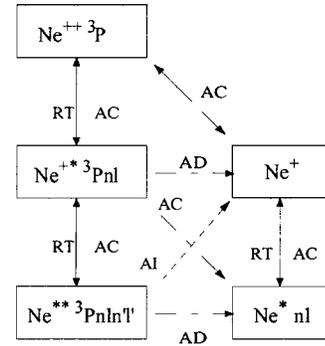

FIG. 2. Electron loss and capture scheme between various Ne^{2+}, Ne$^+$, and Ne states. The various Auger capture (AC), Auger deexcitation (AD), resonant transfer (RT), and autoionization (AI) channels between states are indicated. The excited states actually considered are given in the text.

elastic energy losses in single-scattering conditions.

As in our previous work [9,15], we use a numerical model built along the lines of the one developed by Niehaus and co-workers [8] and successfully used by them to describe some of the characteristics of electron spectra recorded in doubly charged ion neutralization. Figure 3(a) shows the metal+atom or ion states, corresponding to the scheme in Fig. 2. The position of the levels in front of the surface was modeled as described in detail in [8]. This position is determined mainly by the image potential at large distances, whereas at small distances screening effects are taken into account. As may be seen for distances smaller than 2.7 a.u. the $(^3P)3s^2$ state lies above the Fermi level and can autoionize to give the Ne^{+*} $(^3P)3s$ state. In the range of distances considered, the $(^3P)3s$ state lies below the Ne^{2+} state. On the other hand, the higher-lying $(^3P)3p$ Ne^{+*} state can autoionize into the continuum, corresponding to metal+Ne^{2+} for distances smaller than 2.7 a.u. The $(^3P)3p^2$ state remains autoionizing for distances larger than 12 a.u., which, as shown previously [15], explains the small probability of its production.

In the model we solve a set of coupled differential equations for the distance-dependent populations of the various levels for a given perpendicular velocity of the ion moving away from the surface. We assume that resonant and Auger transitions are caused by the overlap of the wave functions of the electron in its initial and final states and that the transition probabilities are determined by the asymptotic behavior of the wave functions. Other details of the model and choice of adjustable parameters for the interactions are outlined in our previous paper [15] and will not be repeated here for brevity.

V. CHARACTERISTICS OF LINE SHAPES

Results of the calculation of the populations of the various levels as a function of atom-surface distance, assuming an initial population of 100% Ne^{+*} $3s$, are schematized in Fig. 3(b) for 5-keV Ne ions leaving an Al surface at 8° (the choice of initial populations was not found to affect the shape of the spectra).

FIG. 4. Dependence of the line shape of the Ne** $2p^4(^3P)3s^2$ state on the exit angle of scattered excited atoms.
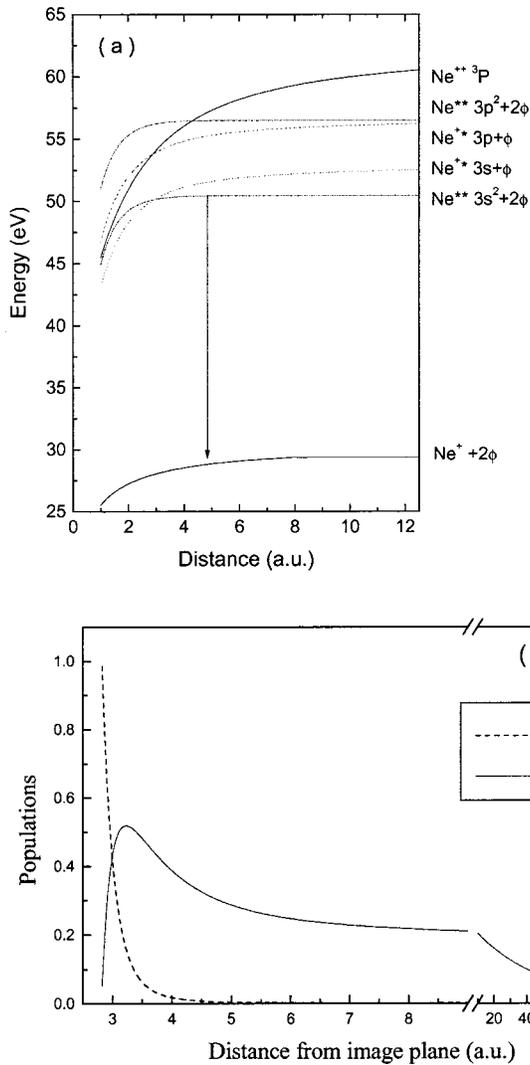

FIG. 3. (a) Potential-energy diagram of the Ne-Al system used in the calculations, represented here for electrons at the Fermi level. The states are identified on the left of the diagram. The thick line represents the Ne^{2+}+metal continuum. (b) Populations of the $(^3P)3s$ and $(^3P)3s^2$ states as a function of the distance from the image plane ($\theta_{ex}=8°$, $E_{ex}=5$ keV).

The initial population of Ne** is strongly attenuated through resonant ionization leading to the production of Ne$^+$* and Ne^{2+}. The final production of Ne** always relies on electron-capture processes. It is for this reason, that for a given set of parameters, the initial state distributions do not affect the spectral line shapes.

Near the surface the Ne** population can be attenuated by Auger deexcitation leading to Ne*. The line shapes of the peaks due to Ne** are determined by the population of the Ne** excited state at various atom-surface distance and the energy separation of the Ne** and Ne$^+$ levels.

Figure 4 shows the calculated line shapes for the $3s^2$ states, for 4°, 8°, and 16° exit angles (for 5 keV ions). As may be seen, the peak has a sharp cutoff at small electron energies, close to the 20.35-eV position, corresponding to the autoionization of a free atom. On the other hand, it has a tail extending to 22.25 eV, corresponding to the maximum en-
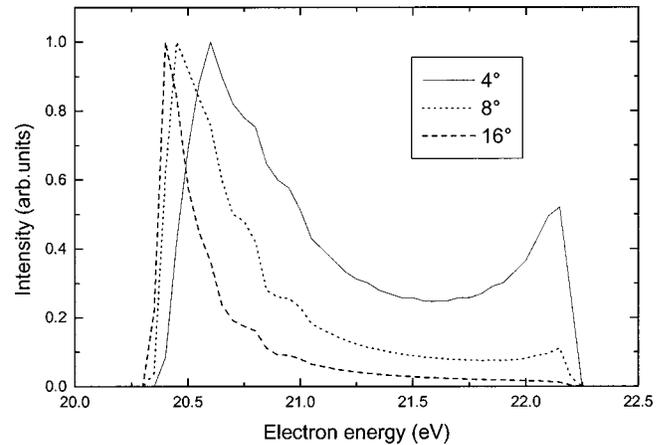
ergy separation of the Ne** and Ne$^+$ levels, for an atom-metal distance of about 2.7 a.u., when the Ne** state can ionize into the continuum Ne$^+$*$3s$+metal.

A very specific feature of the $3s^2$-state line shape is the secondary maximum at about 22.2 eV. This maximum is more pronounced for small exit angles with respect to the surface. This is due to the variation of the population of the state as a function of distance. Close to the surface the population initially decreases rapidly because of Auger deexcitation. At larger distances it is determined only by autoionization. The secondary maximum arises from autoionization *close to the surface* [below 3.5 a.u. see Figs. 3(a) and 3(b)], where the population is large and the Ne**-Ne$^+$ energy separation is also large.

It should be pointed out, in passing, that the secondary maximum described here is shifted to higher electron energies, just like the peaks in electron spectra in doubly charged ion neutralization. In the case of doubly charged ion incidence, autoionizing states are formed on the way ''in,'' as the ion approaches the surface, and their decay occurs close to the surface, where the energy levels of the states are shifted. These peak shifts have been discussed and correctly modeled in the same framework used here in earlier work [8,9].

At intermediate distances ($z<8$ a.u.) the population decreases substantially, but the Ne**-Ne$^+$ separation is still significantly larger than its asymptotic value. Decay in these conditions is responsible for the intermediate, tail portion of the peak. The main portion of the peak, i.e., the region from the maximum to about 21 eV is determined by decay at large distances from the surface (tens of a.u.), a condition that is favored for rough surfaces. The shape of the peak in this region is thus determined by the autoionization lifetime of Ne**.

In general, the line shape obviously depends on the time spent in a given region of atom-surface distance. This effect determines its dependence on the exit angle and hence the perpendicular velocity. For more grazing exit angles, i.e., for small perpendicular velocities, decay occurs closer to the surface and the spectra are broader than at larger exit angles [Fig. 3(b)]. In these conditions the secondary maximum is also more pronounced and can become the dominant feature

of the spectrum. The relative intensity of this maximum gives a measure of the efficiency of Auger deexcitation.

The shape of the modeled spectrum for small angles compares quite well with the shape of the experimental spectra for the flat surfaces. We observe that peaks α and β in Fig. 1 correspond approximately to the secondary maximum in the calculated spectrum. This is clearly visible on the example of the spectrum for 5 keV (middle spectrum), where peak III has a relatively low intensity and thus does not interfere with the tail of the main line peak (peak α). At 20 keV, peak III partially overlaps with structure α, and its corresponding tail overlaps with peak II, altering its intensity. Note that an exact comparison is not possible, because the experimental spectrum corresponds to a sum of spectra due to scattering of ions into various exit angles with respect to the surface and the calculation does not include Doppler broadening effects.

In the case of scattering on a rough, uneven surface, inelastic scattering occurring on surface asperities, step edges, etc., would favor autoionization at larger atom-surface distances (around 8 a.u. and greater in Fig. 3), resulting in the sharper spectra also observed for scattering at larger angles with respect to the surface plane.

VI. CONCLUSIONS

The natural line shapes of peaks in electron spectra due to decay of autoionizing states of Ne, formed in collisions of Ne with Al solid targets, were modeled and investigated experimentally. The modeling takes into account the level shifts of the excited and ionic states of the atom in front of the surface due to image-potential and screening effects, and various resonant and Auger capture and loss and deexcitation processes. It is shown that the electron spectrum generally possesses a peak at energies in the vicinitiy of that corresponding to autoionization of a free atom, as well as a high-energy tail and a secondary maximum. The secondary maximum, associated with decay near the surface, is more pronounced for atoms scattered close to the surface, i.e., in conditions when the exit perpendicular velocity is small. These conclusions are supported by the shape of the experimentally observed spectra and their dependence on surface flatness, assuming that on rough surfaces decay of autoionizing states occurs far from the surface, while on flat surfaces decay occurs closer to the surface where atomic levels are shifted resulting in higher electron energies.

[1] G. Zampieri, F. Meier, and R. Baragiola, Phys. Rev. A **29**, 116 (1984).

[2] S. Lacombe, L. Guillemot, M. Huels, Vu Ngoc Tuan, and V. A. Esaulov, Surf. Sci. **295**, L1011 (1993); Sov. Phys. Izv. Russ. Acad. Sci. **58**, 8 (1994).

[3] V. A. Esaulov, L. Guillemot, and S. Lacombe, Nucl. Instrum. Methods Phys. Res. B **90**, 305 (1994).

[4] R. G. Pregliasco, E. A. Sánchez, O. Grizzi, V. A. Esaulov, and Vu Ngoc Tuan, Phys. Rev. B **53**, R16 176 (1996).

[5] T. E. Gallon and A. P. Nixon, J. Phys. C **4**, 9761 (1992).

[6] F. Xu, N. Mandarino, A. Oliva, A. Bonanno, P. Zoccoli, M. Camarca, and R. Baragiola, Phys. Rev. A **50**, 4040 (1994).

[7] J. Ostgaard Olsen and N. Anderson, J. Phys. B **10**, 101 (1977).

[8] P. Eeken, J. M. Fluit, A. Niehaus, and I. Urazgildin, Surf. Sci. **273**, 160 (1992).

[9] L. Guillemot, S. Lacombe, V. A. Esaulov, and I. Urazgildin, Surf. Sci. **334**, 224 (1995).

[10] O. Grizzi, E. A. Sánchez, J. E. Gayone, L. Guillemot, V. A. Esaulov, and R. A. Baragiola, Surf. Sci. **469**, 71 (2000).

[11] J. Mischler, M. Banouni, C. Benazeth, M. Negre, and N. Benazeth, Radiat. Eff. **91**, 255 (1986).

[12] L. F. De Ferrariis, F. Tutzauer, E. A. Sánchez, and R. A. Baragiola, Nucl. Instrum. Methods Phys. Res. A **281**, 43 (1989).

[13] G. R. Gómez, E. A. Sánchez, and O. Grizzi, Phys. Rev. B **57**, 12 573 (1998).

[14] L. Guillemot, S. Lacombe, M. Maazouz, Vu Ngoc Tuan, V. A. Esaulov, E. A. Sánchez, Yu. Bandurin, A. Daschenko, and V. Drobnich, Surf. Sci. **365**, 353 (1996).

[15] V. A. Esaulov, J. Phys. C **6**, L699 (1994).