

## Crystal azimuthal-angle dependence of excited-state production and core-rearrangement processes in $\text{Ne}^+$ scattering on Al(111)

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We present the results of a study of the azimuthal-angle dependence of  $\text{Ne}^{**}$  excited-state production in  $\text{Ne}^+$  ion scattering on an Al(111) surface. A strong variation in the intensity of  $\text{Ne}^{**}[2p^4(^3P)3s^2]$  and  $\text{Ne}^{**}[2p^4(^1D)3s^2]$ , and most importantly *in their relative intensity*, is observed as a function of crystal azimuth. This is interpreted as being due to a change in singlet-to-triplet *atomic-core rearrangement* of excited scattered Ne projectiles as they move away from the surface. Numerical simulations were performed and these variations in rearrangement rates were assigned to a rapid change in the perpendicular velocity distributions of scattered particles as a function of incidence azimuth. We conclude that nonlocalized atomic rearrangement processes play an important role in the singlet-to-triplet core rearrangement. [S0163-1829(96)50224-9]

Recent experimental studies of ion-surface interactions have revealed the existence of various rearrangement processes<sup>1-7</sup> of atomic states in front of metal surfaces. An example is the process of singlet-to-triplet conversion of  $\text{He}^*$  states.<sup>1,2</sup> Another process of the fundamental importance of understanding the interaction of some of the most common atomic species (open shell atoms) with surfaces was recently discussed in some detail.<sup>3-7</sup> These species are characterized by the existence of several states corresponding to the ground-state electronic configuration of the atom, e.g.,  $N(2p^3: ^4S, ^2D, ^2P)$ ,  $O(2p^4: ^3P, ^1D, ^1S)$ , and this process can result in the rearrangement of these states. The understanding of the mechanisms of this process is of capital importance for a complete understanding of reactions at surfaces involving these species. In this paper we present the results of an experimental and computer-simulation study of the crystal-azimuthal dependence of excited-state production and core rearrangement processes in the scattering of Ne atoms off an Al surface, which allow us to discuss the role of ‘‘nonlocal’’ core rearrangement processes.

This rearrangement process was first invoked to explain the results of inelastic Ne-ion scattering, where the transformation of excited states with a  $\text{Ne}^{++}[2p^4(^1D)]$  core to states with a  $\text{Ne}^{++}[2p^4(^3P)]$  core was considered.<sup>3</sup> Its existence was first inferred<sup>3-7</sup> from a comparison of the characteristics of autoionizing state  $[\text{Ne}^{**}(2p^4(^3P)3s^2)]$  and  $\text{Ne}^{**}[2p^4(^1D)3s^2]$  production in the scattering of Ne ions and atoms on Na, Mg, and Al surfaces, with previously studied gas-phase collisions of  $\text{Na}^+$ ,  $\text{Mg}^+$ , and  $\text{Al}^+$  with  $\text{Ne}$ .<sup>8,9</sup> Production of these was attributed to ‘‘binary’’ collisions of incident Ne and surface atoms and described<sup>3-7</sup> in terms of transitions between states of a transient quasimolecule, using a molecular-orbital correlation diagram as for an atom-atom case.<sup>8-10</sup> In gas-phase collisions of, e.g.,  $\text{Mg}^+$  with Ne, dominant production of the  $^1D$  core states<sup>4,8</sup> is observed, whereas in Ne scattering on solid Mg,  $\text{Ne}^{**}(^3P, 3s^2)$  is dominant. Assuming that in ion-solid collisions the primary electron promotion mechanisms remain valid, it was suggested that the triplet core dominance is due to core

rearrangement.<sup>3-7</sup> Such a process, attributed to an Auger-type two-electron transition between *quasimolecular* states, is known to exist in gas-phase<sup>9</sup> collisions, but is not very efficient. A similar quasimolecular mechanism could also exist here, though it seems doubtful that this could lead to such a strong triplet production. Experimental trends on the energy dependence of excited-state production support a surface-induced enhanced rearrangement.<sup>3,5-7,11</sup> Existing data show that the dominance of  $\text{Ne}^{**}(^3P3s^2)$  corresponds to low collision energies. Recently, we obtained some indication that for low perpendicular exit velocities ( $v_{\perp}$ ), i.e., longer dwelling times near the surface, favor this process.

The above effects were initially tentatively assigned to an enhancement of the quasimolecular rearrangement by metal electrons.<sup>3,5-7</sup> In the case of binary gas-phase collisions, energy conservation considerations only allow for the existence of this process at the crossing point of the molecular states in question. It was suggested that for the case of the (Ne-target atom) quasimolecule at the surface, the existence of metal electrons would allow for the existence of this process from the crossing point to the separation of the molecule, and hence make it more favorable. However this explanation did not seem to be an entirely satisfactory one for two reasons. First, the energetics of this process, i.e., the position of the relevant energy levels of the quasimolecule in front of the surface, is not known. Second, this Auger-type process, involving transitions between molecular states and an electron from the metal band, would only be efficient for the short duration of the separation of the quasimolecule’s constituents, in an internuclear range of about 1 Å ( $\sim 10^{-15}$  sec for 1-keV Ne). Note that this process can be considered to occur essentially ‘‘within’’ the surface, since one would normally consider that the jellium ‘‘edge’’ is located at a distance of half a lattice spacing, i.e., at about 1.5 Å from the metal atom. Therefore it is the above-mentioned dissociation time, dependent on the collision velocity rather than the perpendicular velocity, that should be important. Being short, one can thus question the efficiency of such a process. Other ‘‘atomic’’ processes, which can occur for a large range of

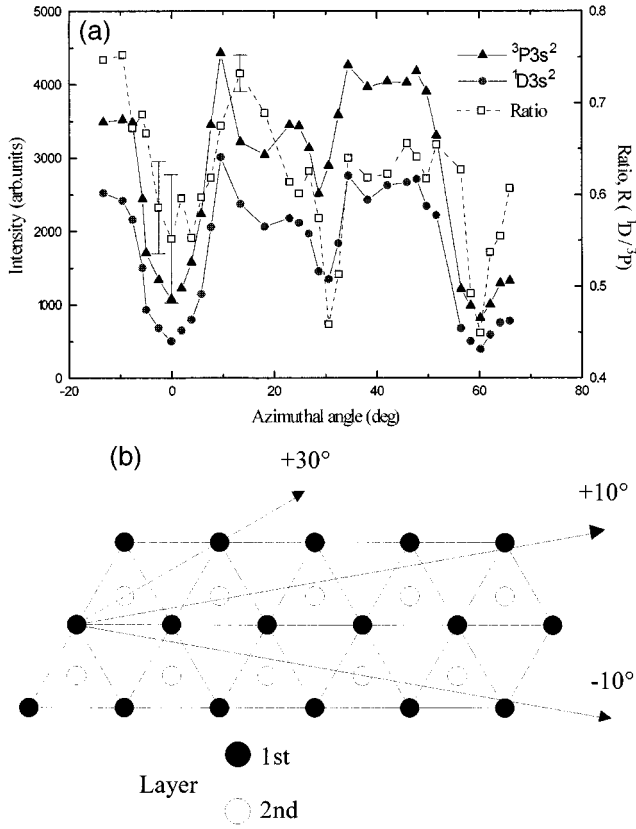
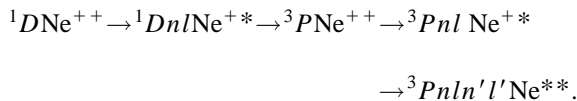


FIG. 1. (a) Electron spectra obtained in 5-keV  $\text{Ne}^+$  collisions with Al(111) for a  $6^\circ$  incidence angle along the indicated azimuths  $\phi$ . (b) Schematic diagram of the scattering geometry.

distances from the collision center, especially in conditions of small-angle scattering with respect to the surface plane, were then proposed. The first of these is a direct Auger rearrangement process involving a transition from the  $(^1D)nl n'l'$  state into the  $(^3P)nl n'l'$  state with the emission of an electron from the solid.<sup>5,11</sup> This will involve electrons from a 3.2-eV region (the  $^1D$ - $^3P$  separation) below the top of the valence band. Another rearrangement process involves a sequence of electron capture and loss processes and has been discussed at length elsewhere.<sup>12</sup> It involves resonant autoionization of a  $^1Dnl \text{Ne}^{+*}$  ion into the  $^3P \text{Ne}^{++}$  plus metal continuum, followed by electron capture, i.e.,



Note that very close to the surface the energy levels of most excited states lie above the Fermi level and hence these are resonantly ionized. Close to the surface the energy levels of the  $(^1D)nl \text{Ne}^{+*}$  states lie below the  $(^1D \text{Ne}^{++}$  plus metal) continuum, but above the  $(^3P \text{Ne}^{++}$  plus metal) continuum limit and hence the above process can occur.

Until now there was no clear experimental evidence in favor of the role of the nonlocal versus local rearrangement effects. All previous studies were performed on polycrystalline targets for which it is difficult to arrive at definite conclusions about scattered ion-atom trajectories that could then be used to discuss the dynamics of excited-state production.

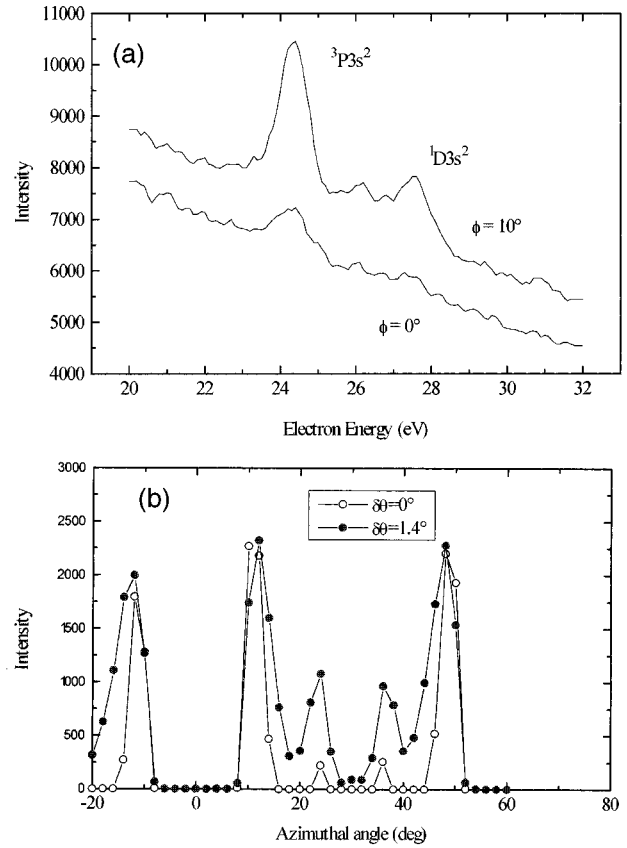


FIG. 2. (a) Experimental intensities of peaks due to autoionizing  $\text{Ne}^{**}$  states and their ratios ( $R$ ). The error bar on the ratio symbolizes the result of various approaches of subtracting a background from the spectra. (b) Computer simulations of the intensities of  $\text{Ne}^{**}$  peaks. A simulation of the effect of convoluting over a  $1.4^\circ$  angular range is indicated.

Here we report results of a study of  $\text{Ne}^{**}$  state production in Ne scattering on Al(111) as a function of the crystal orientation. This is seconded by computer simulations using a modified Marlowe<sup>13</sup> code to include specific features relevant to excited-state formation. This study allows us to discuss in some detail the characteristics of the scattered excited atom trajectories and their effect on the rearrangement process.

Measurements were performed on a setup described elsewhere<sup>14</sup> in the 3- to 10-keV energy range for incidence angles ( $\alpha$ ) in the  $1^\circ$  to  $16^\circ$  range and for a  $80^\circ$  range of crystal-azimuthal orientation ( $\phi$ ). The Al surface was prepared by prolonged grazing incidence, polishing with 20-keV Ar ions, and 5-min annealing cycles at  $500^\circ\text{C}$ . Surface cleanliness was checked by Auger-electron spectroscopy.

Figure 1(a) shows a typical electron spectrum obtained for two crystal orientations (along the  $[1\bar{1}0]$  direction and at  $10^\circ$  from it, see Fig. 1(b)) for a 5-keV  $\text{Ne}^+$  beam incident  $6^\circ$  to the surface plane. The intensity of the peaks drops strongly along the  $[1\bar{1}0]$  channeling ( $\phi=0^\circ$ ) direction. The intensities of the peaks, calculated as the integrals of peak areas after smooth background subtraction, are plotted in Fig. 2(a) as a function of  $\phi$ .

We see that the  $\text{Ne}^{**}(^3P)3s^2$  and  $(^1D)3s^2$  production is weak along the main  $[1\bar{1}0]$  channeling direction ( $\phi=0^\circ$ ) and is most strongly pronounced at  $10^\circ$  from this direction; a

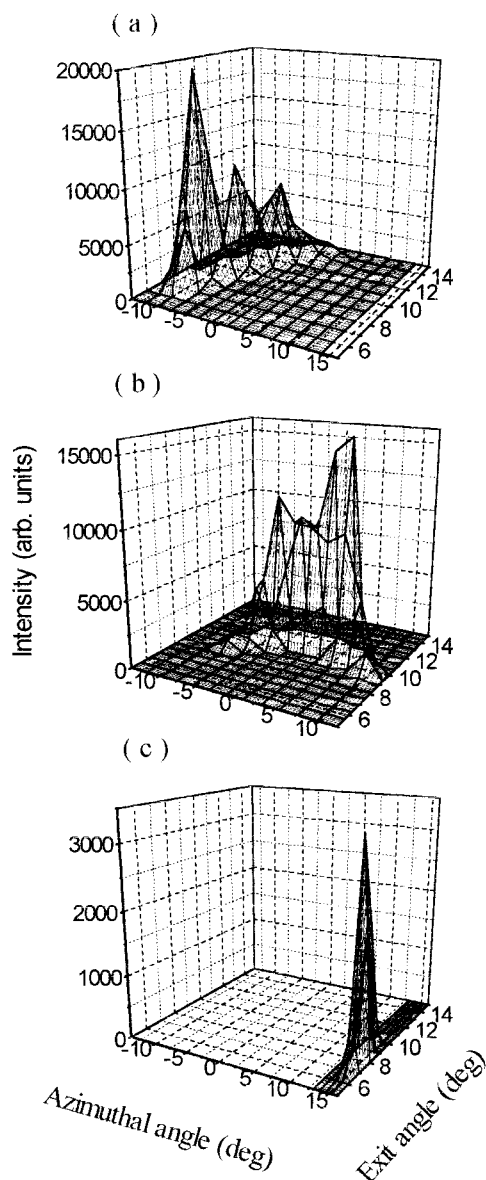


FIG. 3. Simulations of scattered particle intensities ( $6^\circ$  incidence). Incidence azimuth  $\phi$ : (a)  $10^\circ$  top; (b)  $11^\circ$ , and (c)  $14^\circ$ .

secondary maximum is observed close to the  $[1\bar{2}1]$  channeling direction. The  $\text{Ne}^{**}$  maximum intensity is reached for a  $12^\circ$  incidence angle for the  $[1\bar{1}0]$  direction, where the interatomic spacings are the smallest. For other orientations the maximum appears at lower incidence angles.

The most interesting finding is that the *ratio* ( $R$ ) of the  $^1D3s^2$  to  $^3P3s^2$  peak intensities also undergoes variations as a function of  $\phi$ . It has a minimum along the channeling direction (Fig. 2) and reaches a maximum for  $\phi=12^\circ$ , i.e., *not* at the same angle as the  $\text{Ne}^{**}$  intensity maximum. These results suggest that there exist strong differences in the trajectories of the scattered excited particles, which must be at the origin of the variation of the  $^1D3s^2$  to  $^3P3s^2$  peak ratios. It is a strong indication that the  $\text{Ne}^{++}$  core rearrangement ( $^1D\text{-}^3P$ ) processes are not localized at the binary collision center, but occur over a range of distances and are hence strongly dependent on the scattered particle trajectory.

In order to confirm this qualitative conclusion we per-

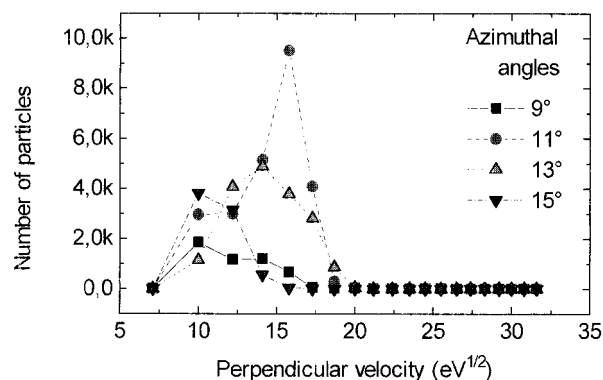


FIG. 4. Perpendicular velocity distributions (see the text).

formed a simulation of these collisions using a two-state quasimolecular model of excitations within the Marlowe code and analyzed scattered particle trajectories. This model will be discussed in detail elsewhere.<sup>13</sup> Briefly, the relevant atom-atom potentials (for ground and excited states) were obtained by comparison with known data on elastic and inelastic angular differential scattering cross sections in the gas phase.<sup>8-10</sup> The Born-Mayer-type ground-state  $\text{NeMg}$  potential is somewhat different from the usual Moliere potential, which was not found to give an adequate description of scattering in the gas phase. The second state corresponds to the excited state of  $\text{Ne}^{**}$  at infinity. Since the couplings between these states are not known, it was assumed that for internuclear distances less than a certain critical distance ( $R_c$ )  $\text{Ne}$  excitation occurs. The second potential was adjusted so as to reproduce gas-phase differential scattering cross sections for inelastic scattering, giving  $R_c=0.85$  a.u. Typical scattering calculations involve following a sequence of binary collisions. If the internuclear distance was smaller than 0.85 a.u., then the excited-state potential was taken in the outgoing trajectory. Only single “close encounter” collisions were considered.

Typically a sample of 0.5 million trajectories was used. The swarm of outgoing trajectories for “inelastic” scattering was then analyzed. The total number of these was taken to be representative of the intensity of excited-state production. This is shown in Fig. 2(b) as a function of azimuthal angle. As may be seen the general trend of the experimental data is correctly reproduced. The maximum  $\text{Ne}^{**}$  intensity is found for  $\phi=10^\circ$ . This direction corresponds to a most “open” direction, a situation where the screening of one atom by another is reduced. In order to model the effect of incident beam divergence, residual surface roughness and a small irregularity in crystal face positioning as a function of azimuthal angle, calculations were performed for a  $1.4^\circ$  incident angular range, thought to be representative of these convoluting effects. The result is a *significantly* broadened dependence, closer to the experimental one. The simulations also correctly indicate that the maximum scattered  $\text{Ne}^{**}$  intensity occurs for a  $12^\circ$  incidence angle.

Figure 3 shows the distribution of exit trajectories as a function of exit azimuth ( $\psi$ ) and angle with respect to the surface plane ( $\theta$ ) for several incidence azimuths. As can be seen very dramatic changes in this distribution occur in a small range of variation of incidence azimuths around  $\phi=10^\circ$ . Note that in all cases discussed here the total scattering angle and hence the final collision energy is the same.

For  $\phi=9^\circ$ , the maximum of the distribution lies for  $\theta=8^\circ$ . This angle rapidly increases to  $13^\circ$  for  $\phi=11^\circ$ . Then, when  $\phi$  increases further to, e.g.,  $14^\circ$ , we again find  $\theta=8^\circ$ . The width of the distribution is also found to change.

Figure 4 presents the distribution of perpendicular velocities. One can see that for  $\phi=11^\circ$  to  $13^\circ$ , corresponding to the maximum in  $R$ , there is a clear increase in the perpendicular velocity component, which thus explains the existence of the maximum in the  $^1D3s^2$  state production observed for these angles in Fig. 2 in agreement with the core rearrangement picture involving an excited atom receding from the surface.

We conclude that our measurements and computer simulations clearly show that the “local” quasimolecular rearrangement processes alone cannot account for the core rearrangement, but atomic rearrangement processes such as Auger and resonant autoionization play a fundamental role in these collisions.

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