Simulation of Core Excitation during Cluster Impacts

M. H. Shapiro

Physics Department, California State University, Fullerton, California 92634

T. A. Tombrello

Division of Physics, Mathematics and Astronomy, California Institute of Technology,
Pasadena, California 91125

Core excitation in Al atoms following the impact of pure Al clusters and composite Al-Au clusters on Au surfaces has been investigated by molecular-dynamics simulation. Core excitation was found to be most probable during the early, compressional phase of cluster impacts. Our simulations predict that a significant fraction of the core-excited Al cluster atoms will decay by atomiclike Auger emission following ejection from the surface, providing a useful diagnostic tool to investigate collisions of cluster ions with surfaces.

Molecular-dynamics (MD) simulations have been used recently to study energy, number-density, confinement-time, ejected-atom, and cascade properties for cluster-ion impacts with surfaces [1–6]. It has been shown previously that the compressional phase of an energetic cluster collision with a metallic target terminates within a few tens of femtoseconds after impact [1,2]. During this compressional phase the number density within the primary impact region of the target typically doubles. It also has been shown that substantial numbers of low-Z cluster atoms are ejected with energies up to twice the bombarding energy *per atom*, when clusters containing low-Z atoms strike high-Z targets. In the present Letter the possibility is investigated that some of these ejected cluster atoms leave the impact zone in core-excited states.

Ion-induced Auger emission from metallic surfaces is a well-established, though infrequently used, technique for surface analysis with beams of single ions [7]. Both MD simulations and experiment have established that the atomiclike Auger lines produced when sputtered, core-excited atoms decay probe the earliest stages of the collision cascade [8,9]. The results reported in this Letter predict that atomiclike Auger lines from the decay of ejected cluster atoms can be used as a probe of the early, compressional phase of cluster-ion collisions with surfaces.

Simulations, using a modified version of the SPUT2 MD code [10], were carried out for 32-, 63-, and 108-atom Al clusters and composite clusters containing 38 aluminum atoms and 25 gold atoms impacting six-layer Au targets containing 1875 atoms. The incoming clusters were normally incident on the (100) surface of the targets. Simulations with pure aluminum clusters were done for incident energies of 0.2, 0.4, 0.6, 0.8, and 1.0 keV/atom. For composite clusters simulations were done for the same *total* cluster energies (i.e., 12.6, 25.2, 37.8, 50.4, and 63.0 keV) as for the 63-atom Al clusters, corresponding to energies *per Al cluster atom* of 0.057, 0.114, 0.171, 0.229, and 0.286 keV, respectively. For computational

simplicity, the incoming clusters were chosen to be crystallite cubes oriented with their (100) faces perpendicular to the direction of incidence. The composite clusters consisted of three layers of aluminum atoms backed by two layers of gold atoms. This structure was used to maximize the effects of reflective collisions rather than to simulate accurately a cluster of molecules. The bulk lattice spacing for aluminum was used for both the pure Al and the composite clusters. Since the bulk lattice spacings for aluminum and gold differ by less than 1%, this choice had almost no effect on the results.

In the SPUT2 code, interactions between atoms are represented by a linear superposition of two-body potentials, and all collisions are treated elastically. A repulsive Molière potential [11] cut off at 2.6 Å was used to represent the interaction between Al and Au atoms, while the Al-Al and the Au-Au interactions were represented by repulsive Molière cores joined smoothly to attractive Morse wells [12] by cubic splines. The parameters for these potentials are summarized in Table I of Ref. [1].

The SPUT2 code was modified to identify hard collisions that would be likely to cause core excitation in one or both of the collision partners. Distance-of-closest-approach (DCA) and time-of-closest-approach (TCA) information was saved whenever the distance between collision partners was 0.6 Å or less. The atoms involved in these hard collisions were flagged for the remainder of the simulation of that particular impact in order to determine the elapsed time between core excitation and the ejection of one or both of the collision partners from the target region.

For each simulation a complete scan of the primary impact zone of the target was made in order to have a representative range of impact parameters, using the same procedure as in our previous simulations [1,2]. Each simulation was terminated at 100 fs in order to minimize the time needed for computation. Since the lifetime of core-excited states in Al is estimated to be less than 50 fs [13], the 100-fs cutoff has little effect on our

results.

A simple critical-distance model was used to estimate the probability for core excitation. The probability for excitation was assumed to be unity for Al-Al collisions in which the DCA was less than 0.44 Å and zero otherwise. This critical distance ($R_c = 0.44$ Å) is equal to the sum of the radii of the maxima in the $2p$-shell charge densities for a pair of aluminum atoms. Such an estimate is consistent with the electron promotion model of Fano and Lichten [14] and with experiment [15]. However, in our simulations we have tracked all collisions (including Al-Au collisions) with DCAs less than 0.6 Å, and more sophisticated excitation models could be applied to our results.

Histograms of distance-of-closest-approach results for the Al_{63} clusters and the $Al_{38}Au_{25}$ composite clusters are shown in Fig. 1. Only those events producing DCAs less than 0.6 Å are shown. Almost all the events shown represent collisions in which both partners were Al atoms. Generally, fewer than 2% of collisions with DCAs < 0.6 Å were between Al and Au atoms. These asymmetric collisions occurred mostly at the higher bombarding energies, and are not included in our core-excitation estimates. It is for this reason that the simple critical-distance criterion could be used to estimate the threshold for core excitation. Obviously, only Al-Au collisions would be possible when individual Al^+ atoms are incident on a gold target. Thus, the yield of Al L-shell Auger electrons from single Al^+ ions on Au would be very small
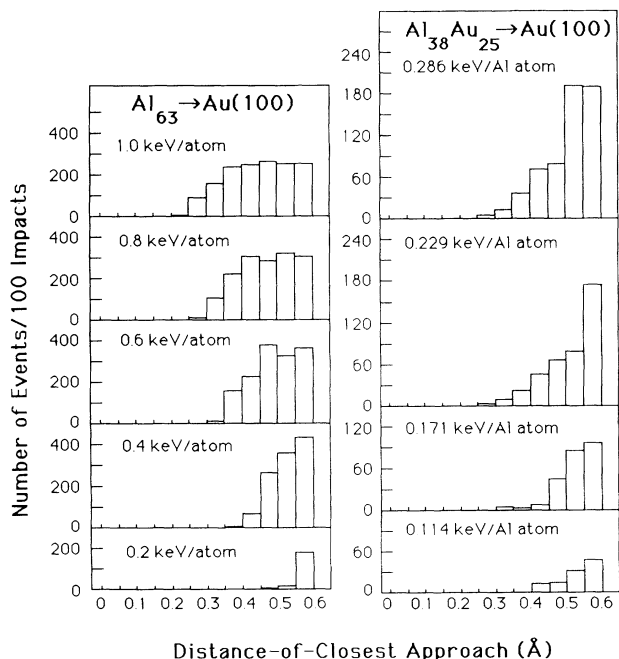
for comparable energies *per incoming atom*. The thresholds for core excitation are at ~0.4 keV/atom for the Al_{63} clusters and at ~0.114 keV/(Al atom) for the composite clusters. Both of these threshold energies are well below the minimum c.m. energy needed to produce a DCA of 0.44 Å in an isolated two-body collision (0.534 keV). However, reflective collision mechanisms in cluster collisions raise the energy of cluster atoms sufficiently to account for these thresholds [1]. Detailed results for the Al_{32} and Al_{108} clusters are qualitatively similar. (Our complete simulation results will be presented elsewhere.)

Plots of the number of hard collisions versus Al cluster-atom energy are shown in Fig. 2 for DCA cutoff values of 0.44 and 0.6 Å for all systems simulated. For the pure Al clusters there appears to be an optimum cluster size for core excitation. The Al_{63} clusters produce close encounters more efficiently than either the Al_{32} or Al_{108} clusters. There probably are too few collision partners available in the 32-atom clusters for most effective production of hard collisions, while in the 108-atom clusters "clearing-the-way" effects [5] by front runners may limit the number of reflective collisions towards the rear of the cluster.
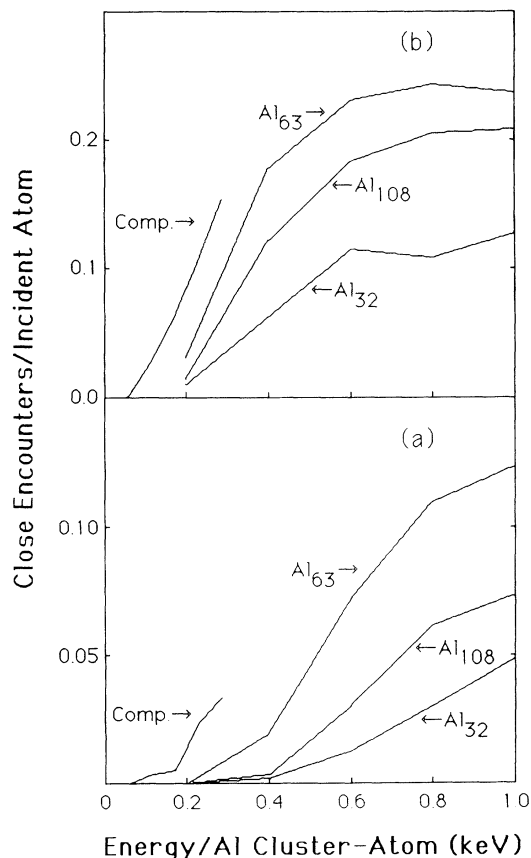

FIG. 1. Distance-of-closest-approach distributions for Al_{63} clusters (left) and $Al_{38}Au_{25}$ clusters (right) impacting Au(100) surfaces. Only Al-Al collisions with DCAs < 0.6 Å are included.

FIG. 2. Number of close encounters *per incident cluster atom* vs the energy of incident Al cluster atoms. (a) Events with DCAs < 0.44 Å. (b) Events with DCAs < 0.6 Å.
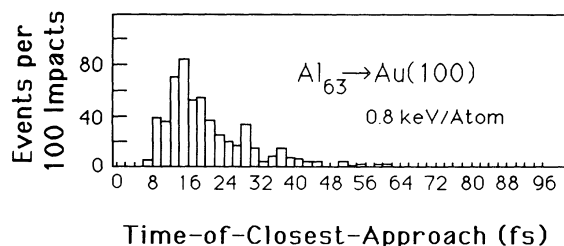
FIG. 3. Typical time-of-closest-approach distribution for Al_{63} clusters impacting on Au(100) surface. Only Al-Al collisions with DCAs < 0.44 Å are included.

FIG. 4. A typical distribution of times elapsing from close encounter (DCA < 0.6 Å) to ejection of Al cluster atoms from the target-cluster system.

A typical histogram of the times of closest approach for events with DCAs < 0.44 Å is shown in Fig. 3. These results are for 0.8-keV/atom Al_{63} clusters. Results for other cases are similar. For the pure aluminum clusters most hard collisions leading to DCAs < 0.44 Å occur within the first 40 fs after the initial contact with the surface, corresponding to the period of maximum compression in the primary impact zone [1,2].

For bombarding energies above the thresholds for core excitation, a relatively large fraction ($\sim 40\%$) of the cluster atoms that experienced hard collisions also were ejected from the cluster-target system shortly after excitation. A histogram of elapsed times between excitation and escape for the 0.8-keV/atom Al_{63} case is shown in Fig. 4. Using this distribution, and assuming a lifetime for Auger decay in the solid of ~ 20 fs (which is within the range of experimental estimates [16]) approximately 43% of the *sputtered*, excited aluminum atoms will Auger decay in vacuum. Since about 40% of all core-excited atoms escape, this implies that about 15% of the core-excited atoms contribute to atomiclike Auger lines. Given the rate of core excitation predicted in Fig. 2(a) for Al_{63} clusters with 0.8-keV/atom energy, there should be roughly 0.4 Auger electron *per incident cluster* that contribute to atomiclike lines. This estimate does not include any correction for nonradiative neutralization close to the target surface [17]. This effect should not reduce our estimate by more than a factor of ~ 2 under the conditions prevalent in cluster bombardment [18]. (To some extent the losses from nonradiative neutralization will be compensated for by the additional core excitation from asymmetric Al-Au collisions that was not included in our estimate.) At our estimated rate experimental detection should be relatively straightforward provided good enough electron energy analysis is used to discriminate against the very large number of low-energy secondary electrons that will be present in cluster bombardment. Thus, observing these L-shell Auger electrons may provide an efficient way of viewing the short-lived, high-
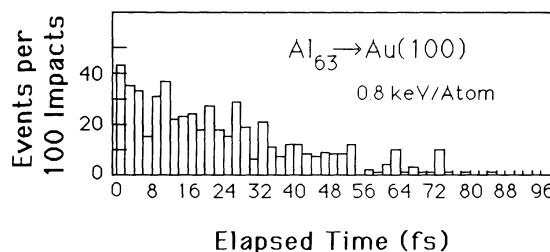
density phase of cluster impacts.

[1] M. H. Shapiro and T. A. Tombrello, Nucl. Instrum. Methods Phys. Res., Sect. B 58, 161 (1991).

[2] M. H. Shapiro and T. A. Tombrello, Phys. Rev. Lett. 65, 92 (1990).

[3] C. Carraro, B. Q. Chen, S. Schramm, and S. E. Koonin, Phys. Rev. A 41, 1379 (1990).

[4] Z. Pan and P. Sigmund, Nucl. Instrum. Methods Phys. Res., Sect. B 51, 344 (1990).

[5] V. I. Shulga and P. Sigmund, Nucl. Instrum. Methods Phys. Res., Sect. B 47, 236 (1990).

[6] V. I. Shulga, Nucl. Instrum. Methods Phys. Res., Sect. B 58, 422 (1991).

[7] Cf. S. Valeri and R. Veruchhi, Nucl. Instrum. Methods Phys. Res., Sect. B 59/69, 37 (1991), and references therein.

[8] M. H. Shapiro and J. Fine, Nucl. Instrum. Methods Phys. Res., Sect. B 44, 43 (1989).

[9] F. Xu, M. Camarca, A. Oliva, N. Mandarino, P. Zoccali, and A. Bonanno, Surf. Sci. 247, 13 (1991).

[10] M. H. Shapiro, T. A. Tombrello, and D. E. Harrison, Jr., Nucl. Instrum. Methods Phys. Res., Sect. B 30, 152 (1988).

[11] G. Molière, Z. Naturforsch. A 2, 133 (1947).

[12] P. M. Morse, Phys. Rev. 34, 57 (1929).

[13] T. D. Andreadis, J. Fine, and J. A. D. Matthew, Nucl. Instrum. Methods Phys. Res. 209/210, 495 (1983).

[14] U. Fano and W. Lichten, Phys. Rev. Lett. 14, 627 (1965).

[15] A. Oliva, A. Bonanno, M. Camarca, and F. Xu, Nucl. Instrum. Methods Phys. Res., Sect. B 58, 333 (1991).

[16] P. M. Citrin, G. K. Wertheim, and M. Schluter, Phys. Rev. B 20, 3067 (1979).

[17] H. D. Hagstrum, Phys. Rev. 96, 336 (1954).

[18] M. Hou, C. Benazeth, N. Benazeth, and C. Mayoral, Nucl. Instrum. Methods Phys. Res., Sect. B 13, 645 (1986).