

## Soft landing and fragmentation of small clusters deposited in noble-gas films

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The collision between small silver clusters ( $\text{Ag}_N$ ,  $N=2-7$ ) and rare-gas films is investigated experimentally as a function of kinetic energy (2.5–50 eV per cluster atom), cluster size, and film material (Ar, Kr, and Xe). Cluster ions are produced by sputtering and size selected by a quadrupole mass spectrometer prior to deposition. The products are studied by UV-visible optical spectroscopic methods. The cluster fragmentation rate is found to decrease with the kinetic energy and when changing the film material from Xe to Kr and Ar. This agrees with previous molecular-dynamic predictions of larger clusters impinging on noble-gas films. In addition we find that the dimer fragmentation rate decreases when the binding energy increases. In order to explain the unexpectedly low dimer fragmentation observed at high kinetic energy, we suggest that after fragmentation partial reaggregation occurs by diffusion of the fragments within the hot region around the impact point. [S0163-1829(98)00735-8]

### I. INTRODUCTION

The synthesis of nanostructured material, which can be seen as solids composed of small units that conserve some of their individual properties after being assembled, is of primary technological importance.<sup>1</sup> Preparation of such material can be achieved by controlled growth of the elementary units on a substrate or by depositing the already formed small units onto a support. In the last case it is crucial to control the deposition process because it is essentially responsible for the structure of the material obtained. One major goal is to find and understand the conditions that allow cluster deposition without fragmentation (soft landing) and without damaging the partly built material. For example, it has been shown experimentally and by molecular-dynamics (MD) simulations that the deposition of  $\text{Ag}_7^+$  on a bare Pd (100) surface leads to strong fragmentation, and to implantation of some of the cluster atoms, for incident kinetic energies as low as 2.8 eV per atom.<sup>2,3</sup> Similarly, the MD study of Hsieh *et al.* of  $\text{Cu}_{13}$  deposition on a Cu surface at 1 eV kinetic energy per atom indicated that 10% of the cluster atoms end up embedded into the substrate, modifying locally the surface structure.<sup>4</sup> However, MD simulations of Cheng and Landman suggested that the addition of a thin rare-gas film on top of the surface should help to deposit the particles nondestructively. They studied the impact of  $(\text{NaCl})_{32}$  and  $\text{Cu}_{147}$  with various rare-gas films,<sup>5,6</sup> and examined in detail the variation of the cluster internal temperature during collision. Soft landing of metal clusters in van der Waals matrices has been obtained by our group,<sup>7</sup> and it has since been confirmed and applied in several experiments.<sup>8-10</sup> Very recently the soft landing of metal clusters on a metal surface has been successfully demonstrated experimentally.<sup>11</sup> The addition of a thin Ar film on top of a Pt(111) surface allowed us to deposit  $\text{Ag}_7^+$  without fragmentation or implantation for an impact energy of 2.8 V per atom. The use of a rare-gas film to softly land metal clusters on a surface seems a promising technique; however, the physical aspects of the process need to be more deeply investigated.

In this paper we present an experimental study of the

fragmentation rate when very small metal clusters are deposited in a rare-gas solid film as a function of the kinetic energy of deposition  $E_d$ , the cluster size, the binding energy of the atoms forming the clusters, and the rare gas composing the film. UV-visible optical spectroscopy is used as a means for the identification of the resulting products. It is shown that the fragmentation rate increases with the kinetic energy of deposition and decreases when the cluster size increases. We also find that the fragmentation rate decreases when changing the rare gas from Xe to Kr and from Kr to Ar, and when the cluster binding energy per atom increases. These results are compared to the collision of particles with a bare metal surface.<sup>3</sup> MD calculations of Cheng and Landman<sup>5,6</sup> serve as a guideline in the discussion.

### II. EXPERIMENT

The experimental setup has previously been described in detail.<sup>7</sup> Briefly, positive metal cluster ions are produced by sputtering, size selected by a quadrupole mass spectrometer, and codeposited with the matrix (film) gas on a cold (12 K)  $\text{CaF}_2$  window. Ion currents are in the nA range and decrease strongly when increasing the cluster size. The deposition area is shown in Fig. 1.

The incoming ions are neutralized with a low-energy

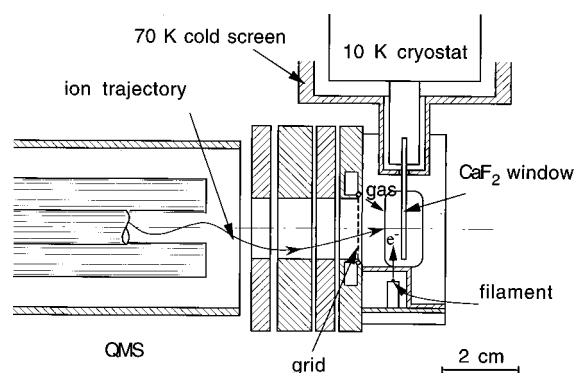


FIG. 1. Detail of the experimental setup in the deposition area.

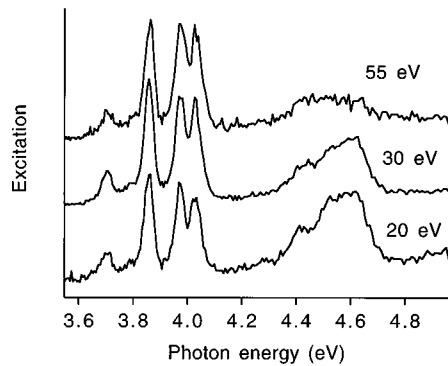


FIG. 2. Excitation spectra of  $\text{Ag}_2^+$  deposited in a Kr matrix at 20, 30, and 55 eV total kinetic energies.

(typically 1 eV) electron beam situated near the cold window. We believe for two different reasons that cluster neutralization occurs when the ions are already inside the matrix or on the rare-gas surface, rather than in the gas phase before reaching the matrix. First, in the case of the dimers, the ionization potentials are large compared to bond energies. Consequently, all the incident dimers would be fragmented if they were neutralized in the gas phase, but this is not what we observe. Second, it has been shown in an experimental setup similar to the one used here that the deposition of Fe ions in nitrogen matrices leads to complexes that were not obtained in earlier attempts from neutral deposits. This has been attributed to the ionic nature of the precursor, which remains charged for a while in the matrix.<sup>10</sup> The electron current has always been maintained far above the minimum current necessary to neutralize the positive charges brought by the clusters. We also find that no influence on the deposition is detected when changing the electron energy in the 0.5–5-eV range.

The deposition kinetic energy is defined as  $E_d = e(U_{\text{grid}} - U_t)$  where  $U_{\text{grid}}$  and  $U_t$  are the voltages applied, respectively, to the last electrode (grid) prior to the deposition, and to the sputtered target,  $e$  being the electron charge. Notice, however, that the kinetic energy of ions produced by sputtering is a distribution centered around 10 eV with a full width at half maximum (FWHM) of typically 15 eV,<sup>12</sup> leading to a kinetic energy a few eV greater than  $E_d$ . High kinetic energy particles are deflected from the ion beam by an energy filter (Bessel box) which also acts as a stop for the neutral clusters. In order to avoid any aggregation in the sample, cluster densities in the matrices are kept close to  $1/10^6$ . Matrix samples are studied *in situ* using standard UV-visible absorption and excitation spectroscopy.

### III. RESULTS

As an example, excitation spectra obtained after deposition of  $\text{Ag}_2^+$  in Kr matrices at  $E_d = 20, 30,$  and  $55$  eV are shown in Fig. 2. The triple structure centered around 3.95 eV corresponds to the known  $^2S \rightarrow ^2P$  excitation of neutral silver atoms in a Kr matrix, whereas the band centered near 4.55 eV was assigned to the  $X \rightarrow B, C$  absorption of  $\text{Ag}_2$ .<sup>7</sup> The presence of silver atoms in the matrix is due to the fragmentation of dimers during the deposition. The spectra clearly show that increasing the deposition energy increases the atomic signal with respect to the dimer one. Since our

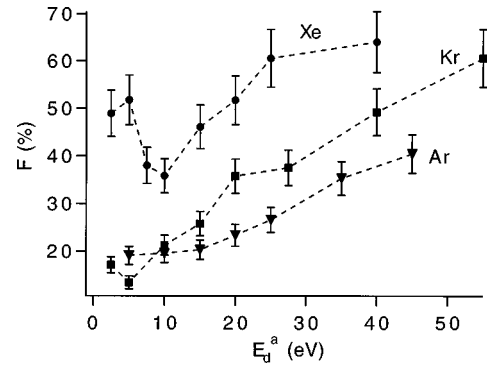


FIG. 3. Silver dimer fragmentation rate as a function of the kinetic energy per atom, when deposited in Ar, Kr, and Xe films.

matrices are highly diluted we have not observed (and do not expect) any features coming from clusters larger than those deposited.

In order to discuss the fragmentation process, we define the fragmentation ratio  $F$  as the ratio between the number of parent clusters that fragment during deposition and the total number of parent clusters deposited. In the particular case of dimer deposition we also define the factor  $Q$  as the ratio between the area under the atom peaks and the dimer band area (centered at 4.55 eV) of the excitation spectra.  $Q$  is related to  $F$  by the relation  $F = (1 + 2Q_0/Q)^{-1}$  where  $Q_0$  is the value of  $Q$  one would obtain for a sample containing the same number of atoms and dimers ( $F = \frac{1}{3}$ ). In principle,  $Q_0$  can be determined using the excitation spectrum of a sample containing only atoms, knowing the oscillator strength of the transitions, and assuming that the deposition efficiencies are nearly the same for atoms and dimers. In practice the uncertainties on the particle densities in the matrix lead to a very imprecise  $Q_0$  value. Another method to determine  $Q_0$  is to use an excitation spectrum obtained after the deposition of trimers at ‘‘high’’ kinetic energy, assuming that the only dissociation channel is  $X_3 \rightarrow X_2 + X_1$ . This hypothesis is supported by the fact that the excitation spectra did not change for kinetic energies of deposition comprised between 50 and 100 eV. In the case of silver in Kr matrices, the mean value of  $Q_0$  obtained from the two methods is  $Q_0 = 1.6 \pm 0.8$ . The estimation of  $Q_0$  for Ar and Xe matrices, done in the same way, gives  $Q_0(\text{Ar}) = 1.1 \pm 0.5$  and  $Q_0(\text{Xe}) = 1.3 \pm 0.6$ , showing that the relative fluorescence yield of  $\text{Ag}_1$  and  $\text{Ag}_2$ , i.e., the value of  $Q_0$ , may depend on the matrix gas.

In Fig. 3 we show the fragmentation  $F$  as a function of the kinetic energy per cluster atom  $E_d^a = E_d/N$  obtained from the excitation spectra of  $\text{Ag}_2^+$  deposited in Ar, Kr, and Xe matrices. It clearly demonstrates that the fragmentation increases with  $E_d^a$  for the three matrix gases. Approaching  $E_d^a = 0$ ,  $F$  does not decrease down to zero but seems to have a minimum between 5 and 10 eV. This is due to the fact that the cluster beam has a kinetic energy distribution (FWHM of around 15 eV) and part of the low-energy side of the distribution is cut off when  $E_d$  is under 15 eV.

Figure 3 suggests that the fragmentation ratio grows when changing the matrix gas as from Ar to Kr and from Kr to Xe. The absorption spectra give, however, more reliable information since the absorption oscillator strengths are less sensitive to the medium than the fluorescence response. Figures

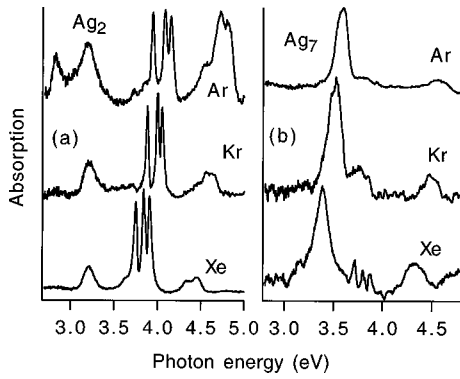


FIG. 4. Absorption spectra of: (a)  $Ag_2^+$  deposited at 20 eV kinetic energy; and (b)  $Ag_7^+$  deposited at 30 eV kinetic energy, in Ar, Kr, and Xe films.

4(a) and 4(b) display the absorption spectra of  $Ag_2^+$  and  $Ag_7^+$  deposited at, respectively,  $E_d=20$  and 30 eV, in Ar, Kr, and Xe matrices. In both cases, the ratio of the integrated atom signal to the integrated parent absorption increases from Ar to Kr matrices, and from Kr to Xe matrices. This confirms the measurements presented in Fig. 3.

In our previous work we have shown that the absorption bands observed in the 225–500-nm wavelength range of  $Ag_N$  ( $N=1-39$ ) embedded in Ar matrices are related to the plasmon resonance predicted by classical theory.<sup>13-15</sup> The integrated spectra correspond on average to 90% of the total oscillator strength of the  $s$  electrons and therefore scale with  $N$ . In Fig. 5 we present the absorption spectra of  $Ag_N^+$  ( $N=2, 3, 5, \text{ and } 7$ ) deposited in Ar matrices at  $E_d=20$  eV for  $N=2, 3$  and  $E_d=30$  eV for  $N=5, 7$ . The  $Ag_3$  spectrum shows clearly a weak atomic feature while the dimer absorption is difficult to identify. The atomic absorption is also discernible in the pentamer spectrum, but it is covered by noise in the heptamer one. Assuming that the channel  $Ag_N \rightarrow Ag + Ag_{(N-1)}$  is the only effective one, a fragmentation ratio can be extracted from those spectra for the four sizes by integrating the area under the absorption peaks. We find  $F=0.3, 0.2, 0.15, \text{ and } 0.1$  for, respectively,  $N=2, 3, 5, \text{ and } 7$ , indicating that for similar kinetic energies the fragmentation ratio goes down when the cluster size increases. This is not surprising, considering that the energy per atom  $E_d^a$  is decreasing. We find that the cohesive energy per atom of a

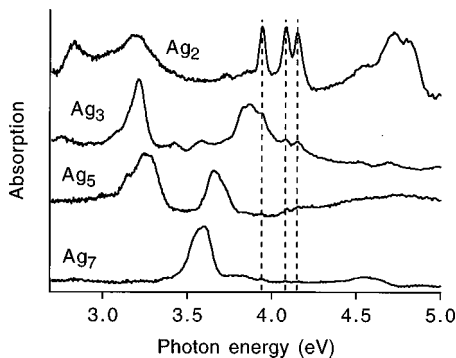


FIG. 5. Absorption spectra of  $Ag_2^+$  and  $Ag_3^+$  deposited at 20 eV kinetic energy, and  $Ag_5^+$  and  $Ag_7^+$  deposited at 30 eV kinetic energy, in an Ar film. The three dotted lines indicate the position of the atomic absorption peaks.

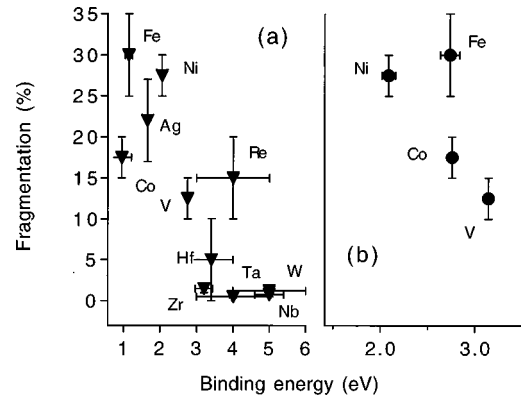


FIG. 6. Fragmentation rate of various dimers deposited in Ar films at a kinetic energy of 10 eV (except  $Fe_2^+$ , which has been deposited in a CO film at 20 eV) vs (a) the neutral dimer binding energy, and (b) the ionic dimer binding energy (see Table I).

cluster increases with size<sup>16</sup> (beside some modulation in the low-size range due to shell effects), which tends to amplify the effect.

The cluster binding energy is obviously a parameter that should also influence the deposition process. Several metal dimers, size selected prior to deposition, have been studied in matrices. In Fig. 6(a) are plotted the fragmentation ratio of those metal dimers (listed in Table I) deposited in Ar at  $E_d=10$  eV vs their neutral binding energies (except  $Fe_2^+$ , which has been deposited in a CO matrix at  $E_d=20$  eV). This figure clearly indicates that the fragmentation ratio decreases as the neutral dimer bond becomes stronger. The binding energies of the corresponding positive dimer ions are only known for  $Co_2^+$ ,  $V_2^+$ ,  $Ni_2^+$ , and  $Fe_2^+$  (see Table I). As revealed in Fig. 6(b), those four points agree with the trend deduced from the neutral dimer binding energies. Note that they would be better aligned if the fragmentation rate of  $Fe_2^+$  had been scaled for  $E_d^a=5$  eV according to Fig. 3, and corrected by the energy gained from the exothermic reaction of  $Fe_2^+$  deposited in CO.

#### IV. DISCUSSION

The deposition process of a particle on a surface is a complex dynamic phenomenon. It can be schematically decomposed into three steps, as MD simulations have shown. The first corresponds to the initial impact between the cluster and the surface, which involves at least one surface and one cluster atom. Then the clusters (or their fragments) are strongly decelerated by friction with the medium as does a bullet into a target. During the deceleration time the cluster temperature increases drastically. Finally, the immobilized clusters (or fragments) start to cool down at a slow rate compared to the heating rate.

A possible approach is to consider these processes as a general reaction in which the reactants are the metal cluster ions, the neutralization electrons, and the matrix atoms; the products being the matrix containing metal clusters (fragmented or not) and some sputtered matrix atoms leaving the surface.<sup>30</sup> In order to predict what will be the reaction products, it is important to understand the process pathway. For a given matrix and cluster chemical composition, the cluster incident kinetic energy per atom  $E_d^a=E_d/N$  is the main pa-

TABLE I. Fragmentation ratio  $F$  of metal dimers deposited in Ar matrices at 10 eV kinetic energy (except  $\text{Fe}_2^+$ , which has been deposited in a CO matrix at  $E_d=20$  eV),  $D_0$  neutral and  $D_0$  ions are, respectively, the experimental neutral and positive ions binding energies.

Species	$F$ (%)	$D_0$ neutrals (eV)	$D_0$ ions (eV)
$\text{V}_2$	12.5 (Ref. 8)	2.75 (Ref. 17)	3.14 (Ref. 18)
$\text{Re}_2$	15.0 (Ref. 19)	4.0 (Ref. 20)	
$\text{Co}_2$	17.5 (Ref. 21)	0.95 (Ref. 20)	2.76 (Ref. 18)
$\text{W}_2$	1.25 (Ref. 22)	5.0 (Ref. 20)	
$\text{Ta}_2$	0.1 (Ref. 23)	4.0 (Ref. 20)	
$\text{Hf}_2$	5.0 (Ref. 24)	3.4 (Ref. 20)	
$\text{Ni}_2$	27.5 (Ref. 25)	2.07 (Ref. 20)	2.08 (Ref. 26)
$\text{Nb}_2$	0.5 (Ref. 27)	5.0 (Ref. 20)	
$\text{Zr}_2$	1.5 (Ref. 28)	3.2 (Ref. 20)	
$\text{Ag}_2$	22.5	1.65 (Ref. 20)	
$\text{Fe}_2$	30.0 (Ref. 10)	1.14 (Ref. 29)	2.74 (Ref. 29)

parameter that controls the collision outcome. In our experiments, where  $E_d^a$  varies between 2.5 and 50 eV, it represents the principal part of the energy involved in the process. Nevertheless, other energy contributions have also to be taken into account: the neutralization energy (typically a few eV), the chemical energy due to the bonding of the metal atoms to the matrix atoms (negligible in rare gases), the clusters initial thermal energy (typically 0.1 eV per atom when created by a sputtering source), and the Coulomb energy between the ion and its mirror charge in the substrate, which tends to accelerate the incoming cluster ions. The Coulomb energy is difficult to estimate in the case of deposition and neutralization in a matrix; it is very likely negligible. For direct deposition on a metal surface it is of the order of 2 eV. The cluster potential energy may also change when the cluster fragments or/and modifies its structure. This also may affect the deposition process, although for small sizes the energy involved should not exceed some eV. During collision, the kinetic energy is converted into cluster vibrational energy (cluster heating) and thermal energy in the matrix. Part of the energy can also be taken out of the system by sputtered film atoms. The relative importance of the energy conversion rate through the different channels is determinant on the issue of the process. Another important parameter is the cooling rate of the cluster and the matrix atoms in its neighborhood; it is related to the heat transport efficiency, and may depend on other processes, such as the evaporation of the matrix. In addition, the cooling channels are interdependent. For example, a strong evaporation of the matrix affects the heat transport efficiency.

The only way of gaining a detailed insight into the different processes occurring during deposition is to refer to molecular-dynamic simulations, using effective potentials. The theoretical work closest to our measurement has been done by Cheng and Landman,<sup>6</sup> which describes in detail the collision between a copper cluster made of 143 atoms and an Ar or Xe liquid film. Although the cluster size in this simulation is large compared to the sizes involved in our study, the qualitative aspects of the collision process revealed by these calculations remain valid in our experimental condition and are important to interpret our results. The evolution of

the cluster temperature and its penetration into the substrate are given for  $E_d^a=1.3$  and 5.3 eV. However, no cluster fragmentation has been revealed by the simulations. The results show that the cluster temperature grows during the deceleration and reaches roughly a maximum when the particle stops. Then the cluster temperature starts to decrease. The time scale of the warmup is typically 1 ps while it is one to two orders of magnitude larger for the cooling. The highest temperatures attained by the cluster when deposited in an Ar film were 850 and 2000 K for  $E_d^a=1.3$  and 5.3 eV, respectively, and 1150 and 4000 K when deposited in a Xe film. Interestingly, the proportion of the initial kinetic energy that is converted into cluster thermal energy is about the same for the two  $E_d^a$  studied, but roughly doubles from Ar to Xe. They also studied the collision of a 32-molecule NaCl cluster with a bare NaCl surface and covered with an adsorbed neon or argon film, at a kinetic energy of 2.72 eV per molecule.<sup>5</sup> Here again, the highest temperature reached by the cluster almost doubles when changing the gas film from Ne to Ar. In the case of the Ne film, they give the spatial gradients of the film density, pressure, and temperature when the cluster temperature has reached its maximum value. At this point the highest temperature reached by the Ne atoms surrounding the cluster is close to 1600 K, and it decreases to 200 K 10 Å away. Cheng and Landman propose a simple model that correlates the energy transfer and redistribution described by the simulation with macroscopic properties of the collision partners, such as mass densities and sound velocities.

One essential parameter given by the MD simulations is the temperature reached by the cluster, which is determined by the energy transfer ratio and the incident kinetic energy. It is closely related to the measured fragmentation rate, and we shall assume here that it increases when the cluster temperature increases. Under this assumption, the qualitative dependence of the fragmentation rate on the matrix gas and on the deposition energy  $E_d^a$  shown by the measurements agrees with the results of Cheng and Landman: both the cluster temperature and the measured fragmentation rate increase with  $E_d^a$  and changing the matrix gas from Ar to Kr and from Kr to Xe. In addition, the dependence shown by the dimer fragmentation rate on the binding energy (Fig. 6) is easily explained within this approach. For the same cluster temperature, weakly bonded clusters have more chance to fragment than strongly bonded ones.

However, some observations are not compatible with this picture. Intriguingly our measurements indicate that the proportion of nonfragmented dimers after deposition is nonnegligible even at kinetic energy per atom  $E_d^a$  as high as 50 eV (see Fig. 2). This cannot be explained by taking into account the width of the kinetic energy distribution in the cluster beam. Speaking in terms of temperature,  $10^4$  K is a conservative estimate of the highest temperature reached by the dimer for such high  $E_d^a$ . Another approach is to estimate the energy transferred to the cluster during collision assuming an energy transfer ratio similar to the ones given by the simulations, which are typically 12% in Ar and 24% in Xe. Hence the energy transferred to a dimer during the collision with a Xe film at  $E_d^a=50$  eV would be 24 eV (extreme case). At such internal energy, it seems clear that a silver dimer (binding energy=1.65 eV) will definitely fragment even if the

time at disposal is very short (of the order of 1 ps, which corresponds to typically 10 dimer vibrations).

We propose that the kinetic energy dependence of the measured fragmentation rate is due to a process that includes some reaggregation. At high kinetic energy, most of the dimers fragment at the beginning of impact. The atoms propagate independently from each other, but are strongly decelerated by the "friction" against the matrix that warms up locally to reach a supercritical state (pressure and temperature are of the order of gigapascals and  $10^3$  K, respectively, as shown by the simulation). Finally, the hot matrix volume containing the two atoms cools down at a low rate (compared to the warmup), allowing the two fragments to recombine. Assuming that all the energy is used to vaporize the matrix, the gas bubble formed around the cluster for  $E_d^a = 50$  eV should not contain more than  $10^3$  rare-gas atoms for Ar and  $5 \times 10^2$  for Xe. Hence, considering the low cluster density in the matrix ( $1:10^6$ ), reaggregation can occur only between atoms of one given cluster.

Direct deposition of metal clusters on a metal surface has been studied by MD simulations and experimentally. In the case of  $\text{Ag}_7^+$  colliding on a bare Pd(100) surface,<sup>2,3</sup> it has been shown that implantation of the cluster atoms into the substrate is crucial to explain the experimental data. At  $E_d^a = 13.6$  eV, about four atoms of the heptamer silver cluster ion are implanted into the first Pd layer and remain grouped, the other three atoms being spread in the adlayer over large distances. At  $E_d^a = 2.9$  eV most of the atoms remain in the adlayer and are well separated from each other. In this case, unless we heat the substrate, the reaggregation process, effective when clusters are deposited into rare gases, does not occur. On one hand, the cooling of the cluster and the neighboring substrate atoms is very rapid, and, on the other hand, the melting temperature of the rare gases is much smaller than that of metals. As an example, Cheng and Landman have shown that the temperature of a  $\text{Cu}_{147}$  cluster that collides a bare Cu(111) surface at  $E_d^a = 5.3$  eV, increases up to 6500 K in around 0.2 ps and then decreases down to 2000 K (considered as the freezing temperature) in less than 1 ps;<sup>6</sup> the temperature of the substrate Cu atoms surrounding the cluster evolves in the same way. In the case of rare-gas films

the simulation indicates that the freezing temperature (typically under 100 K) is reached after more than 20 ps.

Reliable quantitative estimates of the collision of very small metal clusters with rare-gas films are very difficult because it is a highly nonequilibrium system. Thermodynamic variables such as temperature, pressure, heat conductivity, and diffusion constant are not well defined in the nanometer and picosecond scales. In addition, even if the system could be described by quasiequilibrium states, the value of the thermodynamic variables are generally unknown for supercritical states. Therefore, a MD simulation of the collision performed in our experimental conditions are needed to understand more deeply the collision process.

## V. SUMMARY AND CONCLUSIONS

We present an experimental study of the collision between small metal clusters and rare-gas films as a function of the cluster kinetic energy (2.5–50 eV per atom), and the rare gas forming the film (Ar, Kr, and Xe). Silver dimer deposition shows that the fragmentation rate increases with the kinetic energy and changing the film material from Ar to Kr and Xe. Experimental studies of different dimers deposited in Ar also indicate that the fragmentation rate decreases when the binding energy increases. The observed trends are consistent with microscopic descriptions of the collision between medium-size clusters and rare-gas films previously obtained by MD simulations. We also propose that the unexpected low fragmentation rate observed at high kinetic energy can be explained by a reaggregation mechanism (similar to the mechanism that occurs in a cluster aggregation source.) We suggest that most of the dimers fragment at the beginning of the impact. As revealed by MD simulations, the fast deceleration of the fragments overheats locally the film to form a high pressure, temperature, and density region, the diffusion of the fragments inside this hot area gives them some opportunity to recombine.

## ACKNOWLEDGMENTS

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