

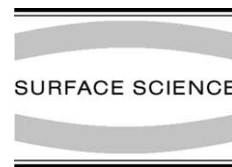


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Theoretical study of mechanisms responsible for emission of highly excited metal atoms

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Abstract

Using a molecular dynamics technique we demonstrate that the formation of holes in the d-shell can be a mechanism initiating sputtering of metastable metal atoms with a closed outer s-shell. The formation of d-holes is a result of electron promotion in the energetic collisions in the cascade developing in solid under fast ion bombardment.
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1. Introduction

Bombardment of solids by keV projectiles results in emission of atomic and molecular species. For clean metal systems the majority of ejected particles is composed of neutral atoms in the electronic ground state. There are relatively small fractions of ions and atoms in electronically excited states. The mechanistic aspects of particle bombardment process, such as the energy and angular distributions of secondary particles are well described in terms of energy and momentum transfer in the collision cascade initiated by the primary ion impact. Electronic processes responsible for the emission of ions and excited atoms, however, are considerably less understood.

The challenge for developing concepts and theoretical models about the excitation process is, in general, hindered by the paucity of sufficient experimental data on one system such that detailed comparisons with theoretical predictions can be made. Recently, however, a series of measurements have been made on properties of atoms ejected in metastable electronic fine-structure states (see Ref. [1] and references therein). The main results obtained are the following:

- The yields of atoms excited to some low-energy metastable states and high-lying states can be anomalously high relative to other states of comparable energy. For example, the population of the $4d^9 5s^2 ({}^2D_{3/2,5/2})$ states of Ag, which lay 4.15, and 3.75 eV, correspondingly, above the ground state have populations up to 6% [2]. In the case of Ni, the $3d^8 4s^2 ({}^3D_2)$ state which lies above the $3d^7 4s^1 ({}^3F_3)$ state has even a greater population [3–5].

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- There can be practically no correlation between the population of different electronic states and the excitation energies [4].
- The kinetic energy distributions of Ni and Co atoms in the $3d^{x-1}4s^2$ states, and Ag and Cu atoms in the $(n-1)d^9ns^2$ states peak at lower energies than the atoms in the states with one electron in the outer s-shell [2,3,5,6].

The electronic processes responsible for formation of the excited states of the ejected particles have been addressed in the past two decades [7–10]. These models for the most part have been proposed in response to new observations, after new data had been taken. Thus they are not capable of predicting the observations mentioned above. A short review of these models is given in Ref. [1]. Here we mention two models being used to describe the $(n-1)d^{x-1}ns^2$ and $(n-1)d^xns^1$ states of Ni, Co, Cu and Ag.

A mechanism, which takes into account the correspondence between the atomic and bulk metal electronic configurations, is resonant electron transfer [11]. According to this mechanism, sputtered atoms leave the surface as positive ions followed by an electron capture from the metal into an excited atomic state. This mechanism was successfully applied for a description of emission of Co and Ni atoms in $3d^{x-1}4s^2$ states of different electronic fine structures [3–5]. The model fails in explaining the formation of the high-energy metastable states such as the $4d^95s^2$ states of Ag lying energetically above the Fermi level. In addition, the characteristics of the kinetic energy distribution of the ns^1 and ns^2 states are not explained.

A variant of the resonant electron transfer model invoking the creation of d-holes within the collision cascade was proposed by Wucher and Sroubek [12] in an attempt to understand the process of emission of Ag atoms in the $4d^95s^2$ electronic state. According to the authors, d-holes are created as a result of excitation of valence-band electrons by the moving cascade atoms. The d-band holes stay localized a sufficiently long time that Ag^+ ions starting to eject can retain the d-hole. These departing ions preferentially capture metal electrons into the s-orbital, thus forming the

atoms in the $4d^95s^2$ states. The longer time the departing ions stay near the surface, the higher probability for them to be neutralized. The authors suppose this process to enrich the low-energy part of the kinetic energy spectrum, thus leading to a narrow energy distribution. The mechanism of the d-holes generation is not completely clear, however. Indeed, the fraction of kinetic energy of the moving atoms that transfers into the electronic subsystem is mainly accumulated by s/p-band electrons, and consequently is quickly dissipated over the entire bulk. The process of conversion of the s/p-band excitations into the d-band takes an additional mechanism not explained by the authors of Ref. [12]. An alternative process of promotion of a well-localized d-electron into the unoccupied part of the conduction band, occurring in close energetic collisions between two Ag atoms, was excluded as not sufficiently contributing to the yield of excited atoms.

In the present work, we show that the observation of excited Ni, Co, Ag, and Cu atoms in the $(n-1)d^xns^2$ electronic configurations suggests that the formation of holes in the d-shell of the atoms participating in the collision cascade evolution can be a mechanism initiating emission of atoms in excited states. Using molecular dynamics simulations we demonstrate that the electron promotion mechanism does significantly contribute to emission of ejected Ag atoms in the $4d^95s^2$ electronic state. The promoted electron remains localized with the ion core in order to shield the uncompensated positive charge of the d-hole. A consequence of such local excitations of the electronic subsystem of the solid is a weakening of the cohesive energy between the atoms in the excited region. This atom and the whole electronic system are not in the ground state. As a result, the cohesive energy of the atom containing a d-hole becomes different from the ground state atoms. The influence of this process on kinetic energy distributions of ejected excited atoms is also studied.

2. Model

The base of our computational model is molecular dynamics simulations used for predicting

the motion of atoms due to energetic particle bombardment [13,14]. Specifically, we model the interaction of Ne, Ar, and Kr atoms with the samples of Ag(111) and a RhAg(111) alloy of equal proportions. Both systems contain about 15 000 atoms arranged in 10 layers.

The interaction among the target atoms is described by the many-body potential constructed by the embedded-atom method (EAM) potential [15], while the projectiles interact with the target atoms through a conventional Molière potential [16]. The EAM potential was chosen as it is possible to treat alloy systems in which the binding energies differ. To follow the cascade evolution in the crystallite, the classical equations of motion are solved numerically for all the atoms in the system.

To simulate d-electron excitations a simple computational model based on the curve-crossing theory of Fano and Lichten is used [17]. This model, implemented earlier in Refs. [10,18], assumes that colliding atoms are excited when the interatomic distance drops below some threshold value r_{th} . We suppose that the promotion of a d-electron to an upper shell occurs with a unit probability when the distance between two Ag atoms drops below $r_{\text{th}} = 1.2 \text{ \AA}$, a value taken from a potential energy curve diagram for the Ag–Ag system in Ref. [12]. This value corresponds to the collision energy of about 140 eV. A decision is made randomly which atom has the d-hole. The d-electron promotion in asymmetric collisions between the projectile atoms and silver atoms occurs at smaller critical distances. The calculation of the potential energy diagrams using the Hartree–Fock method [19], not provided here, gives nearly the same value of $r_{\text{th}} = 0.54 \text{ \AA}$ for the both systems of Ne–Ag and Ar–Ag. For the Kr–Ag system, the value of r_{th} is slightly larger, 0.6 Å. These threshold distances correspond to the following collision energies: 900, 1400, and 1700 eV, respectively.

Once the d-hole has been formed, in principle, it can migrate to other atoms or delocalize. We assume that a d-hole remains localized on an atom unless it undergoes a close collision with another atom. Information on localization of d-holes is based on infinite and non-perturbed solids. In our case, we have d-holes on fast moving atoms. Obtaining the information about localization is,

therefore, a challenge. Some indirect arguments in favor of d-hole localization can nevertheless be given. As it has been shown in Ref. [20], the electronic level localization in collision cascades is a well defined effect taking place even in broad s–p-band metals. Another argument is that more than 90% of ejected particles arise from first layer atoms [21]. Localization of the d-hole should be stronger in surface atoms than in bulk atoms. Consequently we assume that a d-hole can only be transferred to another atom in a resonance process, when two particles approach closer than the critical distance r_{th} . The d-hole, however, can be filled by an electron from the upper electronic shells. Experiments and theoretical calculations of electron–hole excitation and relaxation in transition metal solids have demonstrated that the main channel of d-hole relaxation is an Auger transition from the upper s/p-band [22]. The time dependence of the probability, P , for d-hole survival in the process of Auger relaxation is assumed to satisfy the equation

$$\frac{dP}{dt} = -\frac{P}{\tau} \quad (1)$$

where τ is the lifetime depending on the electronic properties of the solid. The rate of this transition is determined by the formula

$$\frac{1}{\tau} = \frac{2\pi}{\hbar} N_f(\varepsilon) |V_{fi}(r_{12})|^2 \quad (2)$$

where $N_f(\varepsilon)$ is the density of final states at energy ε of an excited electron, V_{fi} is the potential of interaction among the electrons in the metal. A precise calculation of the rate $1/\tau$ is beyond the scope of our work, but a simple estimation can be made in terms of the free electron gas model [23]

$$\frac{1}{\tau} = cn_i^{5/6} \quad (3)$$

where c is a constant and n_i is the local electron density which can be easily obtained from the EAM potential. Finally, we assume that if the ion carrying a d-hole leaves the surface it will be neutralized with the unit probability into its s-orbital, capturing an electron from the metal. Thus, the net effect of creating a d-hole and neutralization into the s-level is the formation of an atom in the excited electronic state, $(n-1)d^{x-1}ns^2$.

3. Results and discussion

Our hypothesis that d-holes can be responsible for excited atoms in $(n-1)d^xns^2$ electronic configurations is based on the following arguments. First, we show that a simple analysis of the time distribution of d-hole formation gives us reasonable yields. Second, we use the excitation model to make direct comparisons of the predicted populations of atoms in excited states with experimental values for three projectiles at two different incident energies. Third, we show for the AgRh alloy that different binding energies give different energy distributions. Finally, we show that if we include a different potential at the time of d-hole formation in the MD simulations we can predict the shift in peak position of the excited state atoms as seen in experiment.

3.1. Simple estimate of yield of excited atoms

The number of ejected atoms containing d-holes can be estimated from the time distribution function, $F(t)$, by the formula

$$N_d \approx \int \exp\left(-\frac{t}{\tau_{av}}\right) F(t) dt \quad (4)$$

where τ_{av} is the average lifetime of the d-holes, $F(t)$ is the distribution function over time intervals between d-hole formation and its departure from the surface. For this simple estimate only we assume the atom has departed the surface when it is 5 Å above the original surface. The function, $F(t)$, is shown in Fig. 1 for molecular dynamics calculations of 1200 trajectories of 5 keV Ar atoms hitting the Ag(1 1 1) surface at a polar angle of 45°.

According to photoemission studies [24,25] and ab initio calculations of the rates of electronic relaxation in metals [26], the average lifetimes τ_{av} of d-holes in Cu, Ag, and Au are relatively long, varying in the range of 20–100 fs. The fraction of atoms containing d-holes, $\eta = N_d/Y_m$ where Y_m is the total atomic yield, was estimated with Eq. (4) for two values of $\tau_{av} = 20$ and 100 fs and using the calculated value of Y_m . The predicted relative yields for excited atoms are 0.03% and 0.9%, respectively; slightly less than the experimental value of the excitation probability 1.6% for 5 keV Ar sputtering of

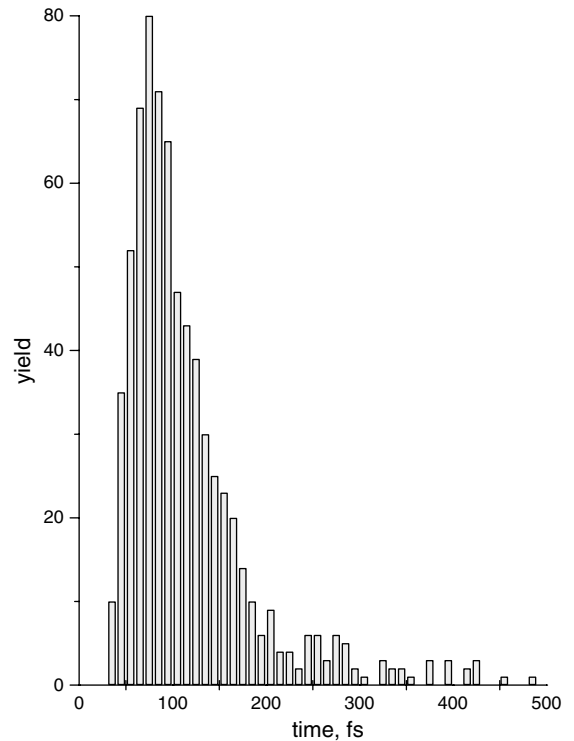


Fig. 1. The distribution function over time intervals between the formation of a d-hole and its leaving the surface, obtained in molecular dynamics calculations of 1200 trajectories of 5 keV Ar atoms hitting the Ag(1 1 1) surface at an angle of 45°.

Ag [2]. The experimental average lifetimes, however, come from measurements of bulk metal samples. As discussed below, our calculations demonstrate that most of the ejected atoms with d-holes arise from the first atomic layer. The excited atoms formed in the surface region experience a lower electron density than the bulk atoms, thus their lifetimes should be longer (Eq. (3)) and the number of excited atoms should be greater than the predicted values of 0.03% and 0.9%. Thus, these values should be considered as lower limits.

3.2. MD calculation of yields of excited atoms

The value of the one parameter c in Eq. (3) must be determined before Eqs. (1) and (2) can be used in the MD simulations. To evaluate c , we monitor the electron density of each atom after a

d-hole has been created for 300 trajectories of 5 keV Ar bombarding the surface of Ag(111). The probability of survival is then calculated for various values of c using Eqs. (2) and (3). A value of $0.15 \text{ \AA}^{5/2}/\text{fs}$ was determined for c by comparison of the results of the calculation for 5 keV Ar with the experimental data [2].

To consider the process of generation and decay of d-holes in greater detail we calculated the fractions of d-hole containing silver atoms emitted under bombardment by Ne, Ar and Kr at incident energies of 5 keV and glancing angle of 45° . In order to approximately represent the polycrystalline target of Ref. [2], we calculated the yields for three main azimuthal directions. In each case we ran 300 trajectories. The evolution of d-holes created in the electron promotion mechanism was treated with Eqs. (1) and (3). The results of the calculations are displayed in Table 1. Although the orientational effect is clearly seen for the total yield of ejected atoms, there is no pronounced dependence of the relative yield of excited atoms on the azimuthal angle. Another feature observed is the higher yield for Ne as compared to the Ar and Kr cases.

To understand the nature of the motions in the solid those give rise to atoms in excited states, and therefore, explain the observations, we traced the trajectories eventually leading to emission of the excited atoms. More than 80% of the trajectories giving rise to d-hole atoms are comprised of sequences of only a few collisions involving the surface atoms. A typical trajectory is shown in Fig. 2a. The d-hole is generated in the energetic collision between the projectile ion and the target atom. The fast recoil atom carrying the d-hole can

either retain it until escaping the surface or transfer it to another atom in an energetic collision. The original atom hit by the projectile eventually turns towards the vacuum after a number of softer collisions. More complex scenarios for excited atom emission, which include collisions of atoms coming from deeper layers, Fig. 2b are also realized, but their contribution to the yield is much less. Thus, the largest fraction of excited atoms comes from the top surface layers. Fig. 3a, where the yield vs. the depth of origin is plotted for 5 keV Ar projectiles, illustrates this finding. The effect also becomes stronger due to the fact that the surface atoms experience lower electron density than the bulk ones. As a result, the d-holes formed on the surface have a greater probability of surviving on their path out of the solid.

The lack of azimuthal dependence of the d-hole yield given in Table 1 can be understood in terms of the mentioned mechanisms. Since the origin of excited atoms is the same as most of emitted monomers, the number of ejected atoms carrying a d-hole should be approximately proportional to the total yield of monomers. As a consequence, the relative yield of excited atoms is practically insensitive to the azimuthal direction of the bombardment. The monomer yield, however, is strongly dependent on the azimuthal angle of incidence.

The higher yield of excited atoms for Ne projectiles as compared to Ar and Xe can be explained by the different contributions to the d-hole yield from direct collisions of silver atoms with projectiles. The cross section for the d-hole formation is the largest for the Ne–Ag pair at the same energy. It can be found, for example, using the

Table 1

Total yields of monomers, the relative yields of excited atoms for three projectiles and three azimuthal directions, $[10\bar{1}]$, $[21\bar{1}]$, and $[1\bar{1}\bar{2}]$, or $\varphi = 0^\circ$, 30° , and -30° , correspondingly

Projectiles	Azimuthal direction of 5 keV beam					
	$[10\bar{1}]$		$[21\bar{1}]$		$[1\bar{1}\bar{2}]$	
	Atomic yield	d-hole yield (%)	Atomic yield	d-hole yield (%)	Atomic yield	d-hole yield (%)
Ne ⁺	1980	2.8	715	3.2	1124	3.0
Ar ⁺	3172	2.1	1643	1.3	2479	1.6
Kr ⁺	4537	2.5	2431	2.0	3589	1.6

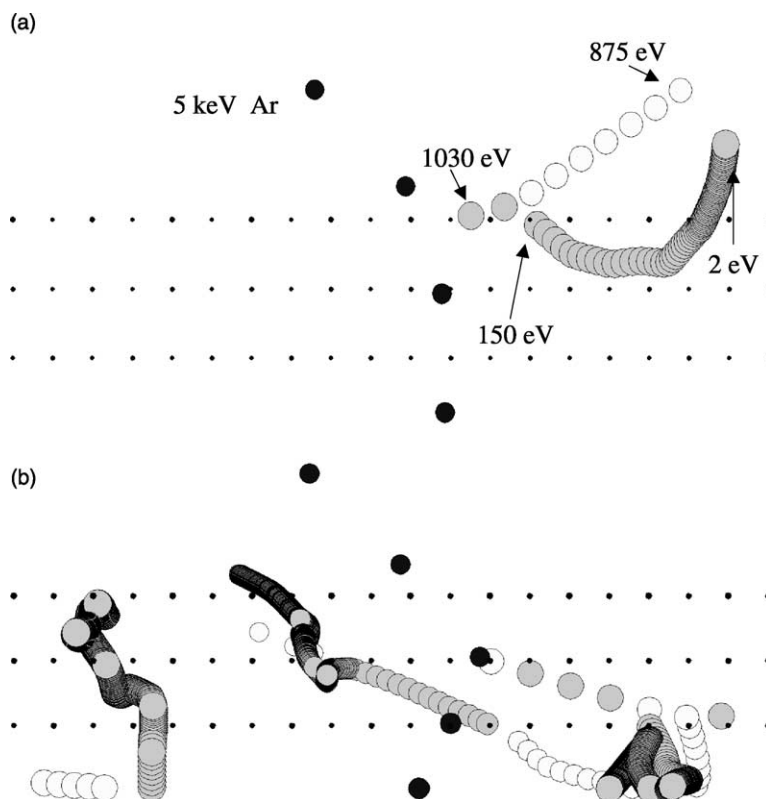


Fig. 2. Pictures of trajectories resulting in emission of excited atoms. Circles indicate the successive positions of moving atoms provided they have the kinetic energy greater than 70 eV. Dark circles show positions of the projectile atom. White circles illustrate movement of silver atoms in the ground state. Grey circles correspond to the positions of excited atoms. Numbers display the kinetic energy of the atom in the positions indicated by arrows.

approximation of the Firsov potential [27], $V(r) = B/r^2$ where B is the constant depending on the atomic numbers of colliding particles. For the projectile energy of 5 keV, the cross section for Ne–Ag is about 1.5 times as much as the cross section for Ar–Ag, and in a factor of 7 greater the cross section for Kr–Ag. It results in the following contributions of collisions with projectiles at 5 keV for the systems in question of 90% for Ne–Ag, 60% for Ar–Ag, and 20% for Kr–Ag.

To demonstrate the dependence of the yield of excited atoms on projectile energy we calculated the fractional yields for three projectiles at the two energies 5 and 15 keV. The same value of the adjustable parameter $c = 0.15 \text{ \AA}^{5/2}/\text{fs}$ was used through the calculations. The results averaged over the three azimuthal directions are given in Table 2 along with the experimental data [2]. The

general tendency, the increase of the probability of the excitation with increasing the primary energy, can be simply explained by the fact that more energetic projectiles deposit the more energy in the crystallite. As a result the number of energetic collisions in the target causing the electron promotion, increases. The agreement of the Ne and Ar values is within 15% of the experimental values [2] while the Kr values have a larger discrepancy, especially for 15 keV. We believe the reason for the Kr discrepancy is the critical distance in projectile–target collisions, which can be calculated from the potential energy diagrams only approximately.

3.3. Kinetic energy distributions

Excited atoms are assumed to form in hard collisions in the cascade. Such collisions are ac-

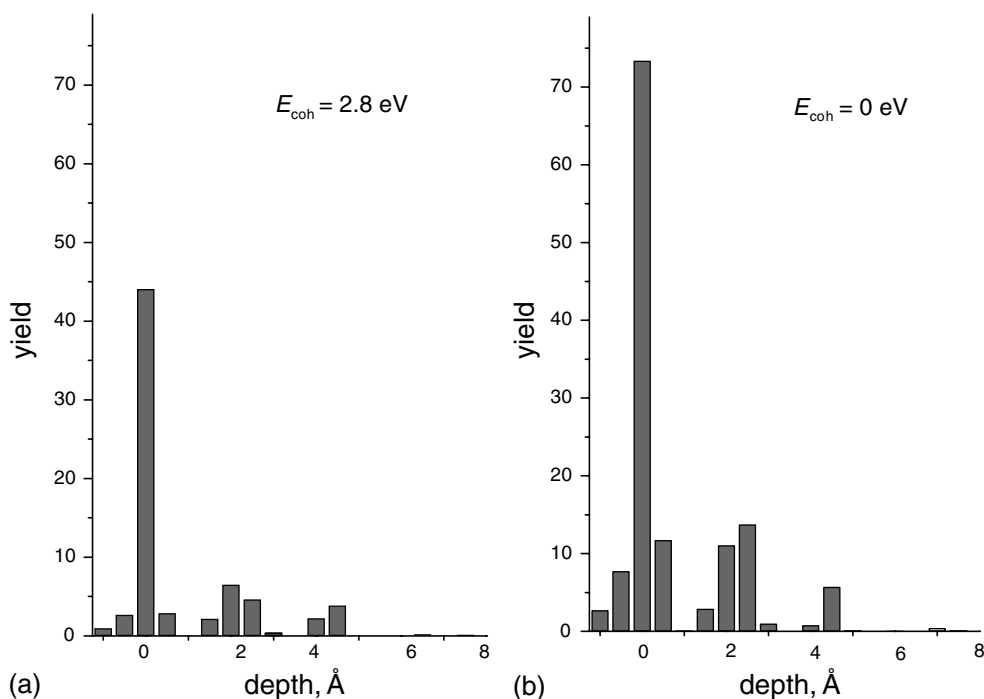


Fig. 3. Distributions of the yield of excited atoms over the depth of d-hole formation. Two cases corresponding to the EAM interaction of atoms carrying d-holes with the rest of the target atoms (a) and the switch of the EAM potential to a repulsive potential, zero binding energy (b) are shown.

Table 2

Relative yields of excited atoms averaged over the three azimuthal directions in comparison with experimental data [2]

Projectiles	5 keV		15 keV	
	d-hole yield (%)	Experimental probability (%)	d-hole yield (%)	Experimental probability (%)
Ne ⁺	2.9	3.0	3.5	3.4
Ar ⁺	1.7	1.6	3.1	3.1
Kr ⁺	1.9	2.5	2.7	5.1

accompanied by large amounts of energy transferred to the excited recoils. As a result, fast atoms should preferentially contribute to the kinetic energy spectra of ejected excited atoms. The calculated energy distribution of excited silver atoms containing a d hole, shown in Fig. 4a, is broader than the distribution of the ground state atoms, and shifted to higher energies. This result is opposite of the observed experimental distributions.

A formation of a d-hole localized at an atom should change the interaction of this atom with the environment. Indeed, the electron promoted to the

s/p-band stays with the parent atom, screening the positive charge of the hole. This electron increases the electron density near the excited atom, weakening the attraction to the system. A precise calculation of the cohesive energy for such an atom is out of the scope of the present work. Nevertheless, some indirect arguments in favor of weakening the bond can be drawn by comparing the binding energies of metal dimers in different electronic states. Adding an extra electron(s) to the outer s-shell weakens the attraction between the atoms. In the limit of the outer shells filled, the interaction is

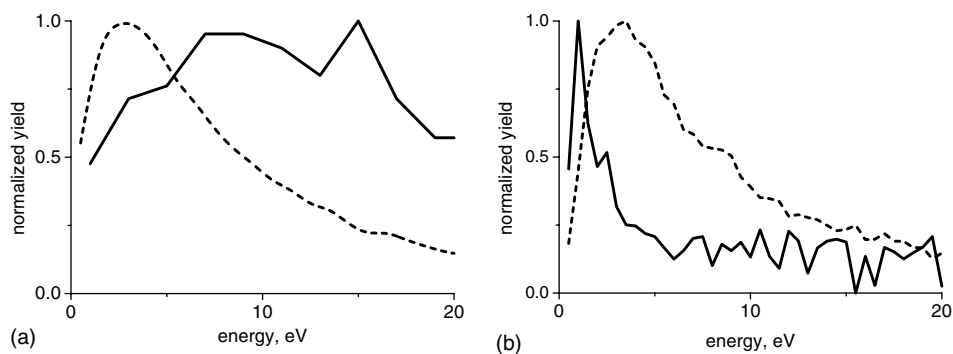


Fig. 4. Angle-averaged kinetic energy distributions of emitted Ag atoms. Dashed lines are for atoms in the ground electronic state. Solid lines are for atoms containing a d-hole for two cases, (a) no correction of the binding energy of excited atoms was made, (b) the interaction potential of excited atoms was switched to the repulsive potential at the moment of d-hole formation.

repulsive for two Ni atoms both in $^3F(3d^84s^2)$ states [28]. The authors state that the d-electrons are located deep inside the atom and are completely screened by the s-electrons. The binding energy of two Cu, Ag and Au atoms both in the $(n-1)d^{10}ns^1$ states drop by 20–30% when one extra s-electron [29,30] is added.

To check the influence of the cohesive energy on the kinetic energy distribution, we model the particle bombardment of a RhAg alloy in equal proportions with random positions of Rh and Ag atoms in the lattice sites. The cohesive energy of Ag atoms is approximately half that of the Rh atoms [31]. Angle-integrated kinetic energy distributions of sputtered Rh and Ag atoms are shown in Fig. 5. It is clearly seen that the distribution for Ag atoms peaks at the lower energy than the distribution for Rh atoms. The absolute yield of less bonded atoms is about three times higher than for the tightly bonded component.

Finally, we simultaneously considered both factors, the energy transfer to the excited atoms at the moment of their formation and the weakening of the bond of these atoms with the environment in order to assess the affect on the kinetic energy distribution of sputtered excited atoms. Unfortunately, the value of the attractive energy for the excited atom in the solid perturbed by a collision cascade is available neither experimentally nor theoretically. In order to demonstrate qualitatively the affect of the bond weakening on the kinetic energy distribution, we used the extreme case. At

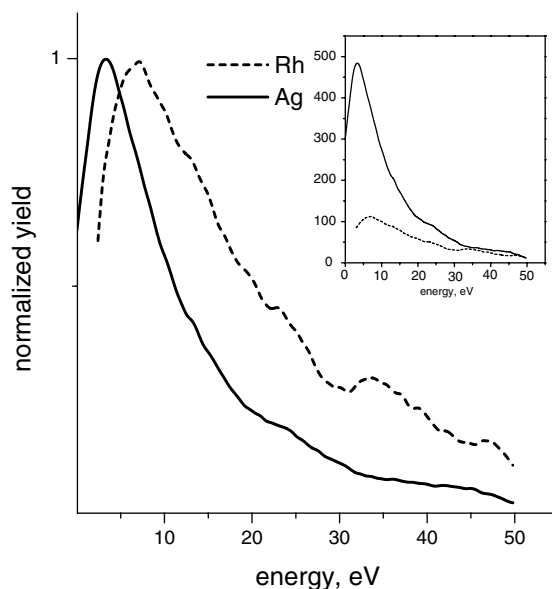


Fig. 5. Angle-integrated kinetic energy distribution of Rh atoms, dashed line, and Ag atoms, solid line, ejected from the RhAg alloy by Ar atoms at initial energy of 15 keV. The number of trajectories was 2700. The absolute yields of the atoms are shown in the inset.

the moment of the excited atom formation, the cohesive energy of the atom is changed to zero from its original value of approximately of 2.8 eV [31]. Any interim values between 0 and 2.8 eV require sophisticated modifications of the interaction potential, and are not useful understanding the qualitative trends.

To perform these calculations the computational model was modified slightly. If a d-hole forms in an atom of the silver crystallite, we switch the EAM potential between this atom and the other atoms to a repulsive exponential potential, $V(r) = D \exp(-\alpha r)$, where $D = 47.35$ keV and $\alpha = 4.84 \text{ \AA}^{-1}$ are the parameters chosen to obtain the best fit between this potential and the EAM potential in the range of distances of $0.65 < r < 1.5 \text{ \AA}$. To minimize the change of the total energy in the system, the switch of the potential is taken at the moment of the closest approach of two atoms. At this point, the influence of the rest of atoms is minimal, and the potential for the interaction of the two atoms can be considered as a pairwise potential with the best possible accuracy.

The energy spectra of emitted excited atoms with zero cohesive energy, $E_{\text{coh}} = 0$, and ordinary silver atoms are shown in Fig. 4b. The distribution for the excited atoms is very narrow with a peak close to zero. The main contribution to the spectrum comes from very slow atoms. The distribution over the depth of their origin, Fig 3b, indicates that these atoms are emitted from the top layers as those in the case of the normal binding energy. The detailed analysis of trajectories shows, that the mechanisms of emission are similar to those shown in Fig. 2. The d hole is transferred from the Ag atom with 1030 eV of energy to another target atom, which has only 150 eV of kinetic energy (Fig. 2a). Practically all this energy is lost in a few softer collisions turning this atom towards the vacuum. Atoms coming from the deeper layers (Fig. 2b) lose kinetic energy on their way to the surface. These atoms have a possibility to escape due to zero evaporation energy. Those atoms accordingly increase the yield of atoms in the excited state by a factor of four. These slow atoms mainly contribute to the energy spectra of emitted particles, shifting the peak of the distribution towards the low energies.

4. Conclusion

The d-hole formation as a result of energetic collisions in the cascade is proposed to be the

mechanism initiating the sputtering of metastable transition metal atoms with the closed outer s-shell. If the d-hole does not decay due to an electron transition from an upper electronic band, the ion carrying it will be neutralized with unit probability into the s orbital at the surface, forming the excited atom. MD calculations of the time distribution of d-hole formation in the Ag(111) crystallite under bombardment by 15 keV Ar atoms gives a reasonable yield of emitted silver atoms in the $4d^9 5s^2$ electronic state.

The formation of a d-hole localized at an atom weakens the bond of this atom with the environment. MD calculations demonstrate that this weakening results in a kinetic energy distribution of the sputtered excited atoms that is narrower than the distribution of atoms in the ground electronic state.

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