Ion-induced emission of excited atoms from (100) surfaces of transition metal single crystals

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The angle-resolved kinetic energy distributions of atoms ejected from Rh{100} and Ni{100} surfaces bombarded with 5.0 keV Ar⁺ ions have been measured for the ground state and two low-lying metastable excited states. The results indicate that the excitation probability varies as exp(− A/av⊥) at high velocities for atoms emitted in so called 'open' electronic configuration (outermost s shell is not fully occupied) and is velocity independent if the configuration is closed. In the former case, the parameter A/a depends on the azimuthal and polar angles of ejection. The observed variations are attributed to the interaction between the substrate electrons and the ejecting atom. At low velocities the excitation probability becomes nearly constant which is attributed to a recently proposed mechanism of excited atom production due to inter-atomic collisions above the surface. The measurements indicate that the relative contribution of this mechanism increases with the excitation energy. The observed dependence of the excitation probability on electronic structure of the emitted atom is discussed in terms of the orbital de-excitation model.

1. Introduction

The emission of excited particles from ion-bombarded metal surfaces has been investigated for a long time. The phenomenon of ion-induced light emission was observed more than a century ago[1]. Since then much experimental and theoretical work has been done to elucidate the mechanism responsible for the production of excited particles. Unfortunately, in spite of these efforts, this mechanism is still far from being fully understood. Partially it is caused by the complexity of the process, but also by the lack of reliable measurements of the kinetic energy and angular distributions. The situation is especially difficult for short-lived excited states. In that case only angle-integrated kinetic energy distributions can be roughly evaluated from measurements of Doppler broadened emission profiles[2,3]. Much more reliable data can be obtained for metastable excited atoms. Doppler Shift Laser-Induced Fluorescence Spectroscopy DSLIF[4-11] or Energy and Angle Resolved Neutral Spectrometry EARN[12-14] obtain kinetic energy distributions with very high accuracy. Moreover, the spectra recorded by the latter technique can also be angle-resolved.

From the theoretical stand point the process of excited atom formation is usually separated into two independent events. In a primary step, the atom is excited via collision-induced inelastic energy transfer[15]. Regardless of details of the primary excitation, it is generally believed that the probability of this process is rather weakly dependent on velocity[16]. Such an assumption is, however, in clear conflict with experimentally observed strong correlation

between these two quantities[7,12-14]. This discrepancy is attributed to the second step of excited atom formation when the excited particle undergoes nonradiative relaxation[17]. The relaxation process has been predicted to vary exponentially with the reciprocal of velocity as:

$$\exp{(-A/av_\perp)}, \tag{1}$$

where a and A are constants and $v_\perp$ is the component of velocity normal to the surface. This expression has been a good representation of numerous experimental results, although deviations at low velocities have also been reported[7,12-14].

In this paper we employ multiphoton resonance ionization to examine the effect of degree of excitation and electronic configuration on the energy distributions of transient metal atoms sputtered in an excited state. We report here the measurements of the velocity dependence of excitation probability of Rh atoms emitted in the first $a^4F_{7/2}$ and the second excited state $a^4F_{5/2}$ from (100)Rh, and the kinetic energy distributions of ground-state a^3F_4 and two low-lying excited-state a^3F_3 and a^3D_2 Ni atoms emitted from (100)Ni bombarded by 5 keV Ar⁺ ions. The $a^4F_{5/2}$ state, like the already investigated $a^4F_{7/2}$ state, is a part of the ground state manifold and lies 0.32 eV above the $^4F_{9/2}$ ground state of Rh. Experiments on rhodium allow us to study the role of the magnitude of excitation energy for energy levels with a similar electronic character. On the other hand, the states investigated in Ni are chosen to belong to different electronic configurations. The a^3F_3 level belongs to a group of states having so

called 'closed' electronic configuration ($3d^8 4s^2$), while the a^3D_2 state belongs to a manifold where electronic configuration is partially 'open' ($3d^9 4s^1$). The terminology 'open' and 'closed' is taken from ref 18. A given configuration is considered as 'closed' if d electrons that determine fine-structure states are surrounded by a closed shell of outermost s electrons. If this condition is not fulfilled the configuration is defined as 'open'.

2. Experimental set-up

The details of the experimental set-up have been described elsewhere[12-14]. Briefly, the measurements are performed in an ultrahigh vacuum chamber (base pressure 1×10^{-8} Pa) equipped with a low-energy electron diffraction and Auger surface analysis system. The combination of a laser resonance ionization with a time-of-flight spectrometry and a position sensitive detector is used to measure simultaneously the kinetic energy and angular distributions of emitted particles.

The Rh and Ni samples are optically polished single crystals of 99.99% purity oriented to within $\pm 0.5°$ of the (100) face by Laue back reflection. The cleaning procedure involves multiple cycles of ion bombardment (6 $\mu A/cm^2$, 30 min) and annealing (900 K, 20 min). A final flash to 1400 K for Rh and 1120 K for Ni results in a sharp bright (1×1) LEED pattern.

3. Results and discussion

3.1. Dependence of excitation probability on the excitation energy.
The velocity of the excitation probability of Rh atoms ejected in the first $a^4F_{7/2}$ and second $a^4F_{5/2}$ metastable excited-state from (100)Rh surface bombarded by 5 keV Ar^+ is shown in Figure 1. In principle, to calculate accurately the excitation probability one should know the populations of excited atoms n^* and the total number of all emitted particles. Since excited particles constitute
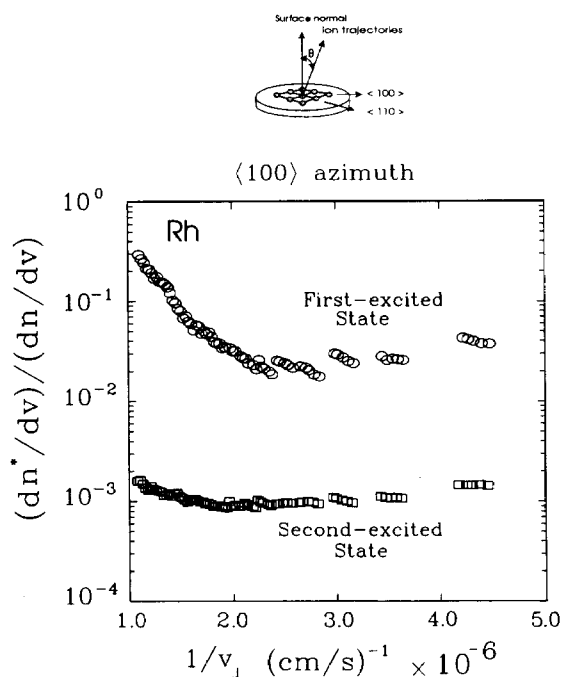

Figure 1. Ratios of the number density of the first-excited state (upper curve) and the second-excited state over that of the ground state $(dn^*/dv)/(dn/dv)$, vs. $1/v_\perp$ for Rh atoms emitted from (100)Rh bombarded by 5 keV Ar^+ ions.

only a minor fraction of all emitted atoms, the latter can be approximated by the number of particles ejected in the ground state n. Under such assumption, the ratio of the angle-resolved velocity distribution of excited atoms to the corresponding distribution of ground-state atoms $(dn^*/dv)/(dn/dv)$, is a good representative for the excitation probability. The excitation probabilities are computed using all particles with polar emission angle $20° < \theta < 30°$. The results for other polar angles are qualitatively similar. As suggested by the functional form of equation (1), the probabilities are plotted on a log scale as a function of $1/v_\perp$. As expected, at high velocity, the ratio indeed approaches an exponential dependence on $1/v_\perp$. However, at low velocities the ratio $(dn^*/dv)/(dn/dv)$ becomes velocity independent. The plots for the first and the second excited states look in principle similar. However, the levelling off of the $(dn^*/dv)/(dn/dv)$ curve occurs at much higher velocity for the second excited state and, hence, this state shows almost no velocity dependence over the measured range.

The behavior of the first excited state has been successfully explained by a collision-induced excitation model described in detail in our previous papers[12-14]. The simulations indicate that the part of the curve that is exponentially dependent on $1/v_\perp$ is easily explained by a simple Hagstrum de-excitation model[17]. The low-velocity part of the curve, however, is influenced by the surface binding energy (the velocity near the surface, where the nonradiative relaxation occurs, is larger than the velocity that we measure), channeling and blocking of exiting atoms in the surface layer and, predominantly, by collisions occurring among them over the surface. The contribution from excitations occurring above the surface might, at first, seem to be unimportant because the probability of such a process is very small. However, because excitation occurs outside the region of effective atom–surface interaction, the survival probability is almost a unity and, in result, the overall excitation probability is not negligible. This mechanism may be visible only when the overall excitation probability is small, which is in the velocity region where most of the atoms excited at and below the surface are quenched by the nonradiative relaxation. The results indicate that this process becomes more significant for excitations to higher lying states.

3.2. Effect of electronic configuration.
A few years ago Craig and coworkers published an orbital de-excitation model[18]. The model was proposed to describe some aspects of excited atom formation in ion-bombarded transition metals. These elements are specific. Contrary to other materials, in transition metals low-energy excitations are caused by promotion of electrons from internal d-shell. Craig *et al* classify all excited transition metal atoms according to their electronic configurations. To the first group they count excited particles in which d electrons are surrounded by a closed shell of s electrons. For the members of this group d electrons are supposed to be shielded from the interaction with the surface. In result, the nonradiative relaxation is hindered and the kinetic energy distribution should in principle preserve its initial shape. On the other hand, for partially shielded and exposed cases, the final-state population and the energy distribution reflect both the initial excitation process and the de-excitation as the atoms depart from the surface region. As is shown in Table 1, most of the previously investigated low-excited (< 1 eV) metastable atoms had 'close' electronic configuration. In result, the kinetic energy distributions of these particles were the same as for the ground-state atoms. The only experiment performed so far with low-excited metastable atoms having

Table 1. Correlations between the type of electronic configuration and experimentally observed broadening of kinetic energy distributions of metastable excited atoms as compared to the ground-state spectra

Element	Electronic configuration	Type	Excitation energy (eV)	Broadening	ref
Ba	$5d^1 6s^1$ ^1D	open	1.40	Yes	7
	$5d^1 6s^1$ ^3D	open	1.20	Yes	7
Fe	$3d^7 4s^1$ ^5F	open	1.30	Yes	8
Ti	$3d^2 4s^2$ $^1D_2$	close	0.90	Yes	10
Rh	$4d^8 5s^1$ $^4F_{7/2}$	open	0.19	Yes	12–14
	$4d^8 5s^1$ $^4F_{5/2}$	open	0.32	Yes	
Fe	$3d^6 4s^2$ $^5D_3$	close	0.08	No	8, 9
	$3d^6 4s^2$ $^5D_1$	close	0.16	No	9
Ti	$3d^2 4s^2$ $^3F_3$	close	0.02	No	10
	$3d^2 4s^2$ $^3F_4$	close	0.05	No	10
Zr	$4d^2 5s^2$ $^3F_3$	close	0.07	No	5
	$4d^2 5s^2$ $^3F_4$	close	0.15	No	5

'open' configuration were done on Rh[12-14]. They show that the energy distributions of ground and excited state atoms are indeed different.

To verify the predictions of the orbital de-excitation model[18] we have performed the experiment with Ni. Nickel has several metastable states which, on the one hand, can be probed by our laser system, and, on the other hand, have 'open' and 'close' electronic configurations. In result, for Ni we have a unique opportunity to investigate on one system the effect of both types of configuration on the shape of kinetic energy distributions.

The angle-integrated energy distributions of Ni atoms emitted in the ground-state a^3F_4 and two low-lying excited states a^3F_3 and a^3D_2 from 5 keV Ar^+ bombarded (100)Ni surface are shown in Figure 2. The a^3F_2 level belongs to a group of states having so called 'closed' electronic configuration ($3d^8 4s^2$), while the a^3D_2 state belongs to a manifold having partially 'opened' electronic structure $3d^9 4s^1$. The highest lying a^3D_2 level has the excitation

energy of barely 0.17 eV, therefore, according to the excitation energy classification, all energy spectra should be the same. It is evident that the energy distribution of the a^3D_2 state is much broader than the kinetic energy spectrum of the ground-state atoms. At the same time, the kinetic energy distributions of atoms ejected in a^3F_3 and a^3F_4 are virtually the same.

The above observations indeed support the orbital de-excitation model. However, it may be a little risky to draw final conclusions based on just two measurements. Therefore, we are currently investigating the polar angle and kinetic energy distributions of four other metastable excited states in Ni. Two of them have 'open' and two other 'closed' electronic configurations. We expect that the results of these measurements will enable us to definitely correlate the excitation probability with the type of electron structure. The experiments are on the way and the results will be published later.

4. Summary

We employed multiphoton resonance ionization to examine the effect of degree of excitation and electronic configuration on the energy distributions of transition metal atoms sputtered in an excited state. The velocity dependence of excitation probability of Rh atoms emitted in the first and the second excited state $a^4F_{5/2}$ from (100)Rh, and the kinetic energy distributions of the ground-state a^3F_4 and two low-lying excited-state a^3F_3 and a^3D_2 Ni atoms emitted from (100)Ni bombarded by 5 keV Ar^+ ions have been measured. The experiments on rhodium allow us to make a detailed study of the role of the magnitude of excitation energy for levels with similar electronic character. On the other hand, the states investigated in Ni were chosen to belong to different electronic configurations. The measurements indicate that the excitation probability of first and second excited-state Rh atoms have an $\exp(-A/av_\perp)$ dependence at high velocity. At low velocity the excitation probability is almost velocity independent. The deviation point occurs at much higher velocity for the second-excited state than for the first-excited level. This result is consistent with the collision-induced excitation model and indicates that a role of excitations due to collisions over the crystal surface increases with the degree of excitation. The kinetic energy distribution for Ni atoms emitted in the a^3F_3 state ('closed' electronic configuration) is found to be virtually identical to the spectrum of ground state atoms, whereas the energy distributions of excited atoms emitted in the a^3D_2 level ('open' electronic structure) is broader. No correlation has been observed between the shape of energy distribution and the excitation energy which indicates that the type of electronic structure rather than the excitation energy is a primary factor in determining the energy spectra.
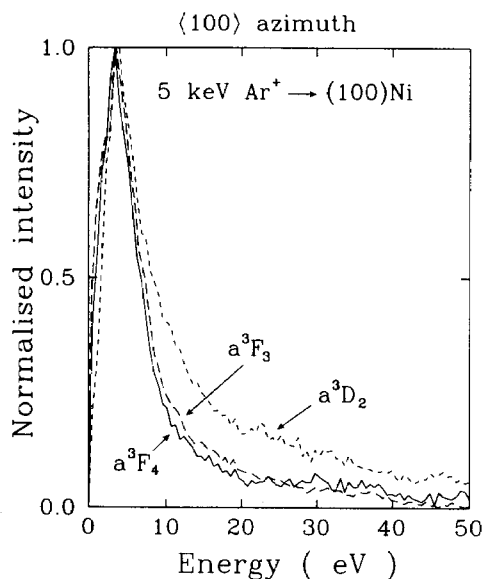
Figure 2. Angle-integrated kinetic energy distributions of Ni atoms emitted in the a^3F_4 ground-state (solid line), the 'close' a^3F_3 (broken line) and the 'open' a^3D_2 (dense broken line) excited states from (100)Ni surface bombarded by 5 keV Ar^+ ions. The plots are normalized to the maximum intensity.

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