Radiation-induced bound-free transitions of surface atoms

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We investigate radiation-induced bound-free transitions of surface atoms from a bound state in a potential well to a continuum in the absence of electron excitations in the system. The bound state corresponds to the ground electron state of the particle-surface system. For an electron beam, the transitions result from inelastic scattering of electrons by surface atoms. A formula for the differential cross section of the transition is obtained. In a field of an electromagnetic wave, the transitions are due to photon absorption by a bound atomic particle. This process is a photoeffect for surface atoms. An expression for the transition cross section for single-photon absorption is obtained. The results are compared with experimental data.

1. INTRODUCTION

Radiation-induced desorption of atoms from a solid surface is presently considered as a multistage process induced by elementary electron excitations in the particle +surface system.[1–3] Electron excitation of a particle results in its transition to the repulsive branch of potential energy, corresponding to an excited electronic state of the system. The subsequent stage of the process is determined by particle motion along the repulsive branch whereby it can acquire the energy necessary for its detachment from the surface. When a particle is moving, modification of its charge state and energy dissipation are possible near a solid surface.[1,2,4] Elementary electron excitation may result both from transitions of valent electrons[5,6] and from ionization of core levels with their subsequent Auger decay.[7]

A difficulty typical of available theories of desorption consists in the following. Electron or photon radiation may induce desorption of surface atoms, if the excited state has a long lifetime,[4,8,9] since the motion of an atomic particle should be sufficiently rapid to match electron deexcitation. However, calculated and experimental values of single-electron excitation lifetimes are 1–10 fs for both an excited atom+surface system[8,9] and a metal surface.[10] On the other hand, a typical time of motion of a particle being desorbed in a potential field near a surface is of the order of 0.1 ps.[1,4,8]

In view of this difficulty, much attention has been paid recently to investigation of multielectron excitations in a system, at which longer lifetimes of atomic particles in excited electron states are possible.[1,2,7,11] Ionization of core electron levels is generally considered as the initial excitation, with subsequent deexcitation through the Auger process.

In the present work, a theory of interaction between atoms on a solid surface and incident radiation is developed. The theory is based on the channel of bound-free transitions of a surface atom from a bound state in a deep potential well corresponding to the electronic ground state of the system to a continuum in the absence of electron excitations in the system.

For an incident electron beam, bound-free transitions result from inelastic scattering of electrons by surface atoms with the electron configurations conserved. Here, the interaction potential in a collision between electron and surface atom is determined by the central field of the nucleus screened by atomic electrons. In the case of an incident electromagnetic wave, these transitions are induced by photon absorption by a bound atomic particle on the surface. This process is essentially a photoeffect for surface ions.

Note that, for the investigated interaction channel, initial electron excitations in the system are not necessary. The bound-free transitions are made possible by the particle-surface bond and result from interaction of radiation directly with the nucleus of a surface atom screened by atomic electrons.

The structure of the paper is as follows:

In Sec. 2, we investigate the channel of bound-free transitions of surface atoms interacting with an electron beam normally incident on the surface. An expression is derived for the differential cross section of the transition to the continuum. The expression corresponds to the electron ground state of the system. In Sec. 3, bound-free transitions of surface ions in the field of an incident electromagnetic wave are investigated. An expression is obtained for the photoeffect cross section for surface ions in the case of single-photon absorption. The results are compared with available experimental data on radiation-induced absorption.

2. ELECTRON-BEAM-INDUCED BOUND-FREE TRANSITIONS

2.1. The amplitude of a bound-free transition

The Hamiltonian for surface atoms interacting with an incident electron beam can be represented in the form:

$$H=\sum_{\lambda}\varepsilon_{\lambda}c_{\lambda}^{+}c_{\lambda}+\sum_{k\sigma}\varepsilon_{k}a_{k\sigma}^{+}a_{k\sigma}+\sum_{\substack{k,k_1,\sigma\\ \lambda,\lambda_1}}V_{ei}(k,k_1;\lambda,\lambda_1)a_{k\sigma}^{+}a_{k_1\sigma}c_{\lambda}^{+}c_{\lambda_1}. \quad (1)$$

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Here, $a_{k\sigma}$ and $a_{k\sigma}$ are the operators of creation and annihilation of an electron with wave vector k, spin σ, and energy ε_k; c_λ^+ and c_λ are the operators of creation and annihilation of a particle in the state $|\lambda\rangle$ with energy ε_λ. The states $|\lambda\rangle$ include both bound states at a surface and continuum states.

The matrix element of particle transition from the state $|\lambda_1\rangle$ to the state $|\lambda\rangle$ resulting from the inelastic scattering of an electron from the incident beam with conserved electron configuration of a surface atom $|\psi_e\rangle$ is

$$V_{ei}(k,k_1;\lambda,\lambda_1)$$
$$=\langle\psi_e|\langle k\sigma|\langle\lambda|V_{ei}(\mathbf{r},\mathbf{R},\{r_e^j\})|\lambda_1\rangle|k_1\sigma\rangle|\psi_e\rangle, \qquad (2)$$

where $\mathbf{r}$ is the electron radius-vector: $\mathbf{R}$ is the particle radius-vector measured from the position of the potential-well minimum: $\{r_e^j\}$ is the set of atomic-electron coordinates measured from $\mathbf{R}$; $V_{ei}(\mathbf{r},\mathbf{R},\{r_e^j\})$ is the interaction potential between an incident electron and a central field of a nucleus screened by atomic electrons.

In the initial state $|\lambda_0\rangle$, a particle is in the ground state in a deep potential well near the surface. The final state corresponds to a continuum state for a free particle. This state is specified by a wave vector $\mathbf{g}$ and a quantum number n.

The amplitude of a bound-free transition $B(\mathbf{g}n;\lambda_0)$ is associated with the S-matrix determined from (1) in the interaction representation by the following relation:

$$-2\pi i\delta(E_f-E_i)B(\mathbf{g}n;\lambda_0)=\langle f|\langle\mathbf{g}n|S|\lambda_0\rangle|i\rangle, \qquad (3)$$

where $E_i=-\varepsilon_b+\varepsilon_i$; $E_f=\varepsilon_{gn}+\varepsilon_f$; ε_b is the particle bond energy in the continuum state $|\mathbf{g}n\rangle$; ε_i and ε_f are the electron beam energies in the initial $|i\rangle$ and the final $|f\rangle$ states, respectively.

In the experiments on induced desorption, electron beams with electron energy $\varepsilon_{k0}\leqslant 10$ keV are generally used. This is much greater than the bond energy of a surface atom $\varepsilon_b\simeq 1$ eV. Eqs. (1)–(3) make it possible to obtain an expression for the transition amplitude in any order in the interaction operator. We restrict ourselves below to the first order in V_{ei} for the amplitude, since one of the general laws of induced desorption is that the desorbed particle flux be proportional to the incident radiation flux, if the latter does not heat the surface.[2]

2.2. The cross section of a bound-free transition

From (1) and (3) we get for the differential cross section of a bound-free transition of an atomic particle:

$$\frac{\partial\sigma_t}{\partial\varepsilon_g\partial O_g}=2^{-2}\pi^{-2}\frac{M^{3/2}m^{1/2}}{\hbar^4}\left(\frac{\varepsilon_g}{\varepsilon_{k0}}\right)^{1/2}\Omega_i\Omega_e$$
$$\times\sum_{kn}|V_{ei}(k,k_0;\mathbf{g}n,\lambda_0)|^2\delta(\varepsilon_{k0}-\varepsilon_k-\varepsilon_b-\varepsilon_{gn}). \qquad (4)$$

Here, M is the particle mass; m is the electron mass; Ω_i and Ω_e are the normalization volumes for the wave functions of a particle and an electron in the continuum, respectively; ε_k is the energy of the scattered electron.

Consider now the interaction potential for the case of a collision between an electron from the incident beam and a surface atom. This potential can be divided into two parts corresponding to a nucleus with atomic number Z and an electron cloud of a particle.[12,13] Using the plane-wave approximation for single-electron states of the beam, we get from (2) for a transition matrix element

$$V_{ei}(\mathbf{k},\mathbf{k}_0,\mathbf{g}n,\lambda_0)=\frac{4\pi e^2}{\Omega_e\Delta k^2}\cdot(Z-Q(\Delta\mathbf{k}))$$
$$\times\langle\mathbf{g}n|\exp(i\Delta\mathbf{k}\mathbf{R})|\lambda_0\rangle, \qquad (5)$$

where $\Delta k=k_0-k$; $Q(\Delta k)$ is the atomic form-factor:

$$Q(\Delta\mathbf{k})=\left\langle\psi_e\left|\sum_j\exp(i\Delta\mathbf{k}\mathbf{r}_e^j)\right|\psi_e\right\rangle, \qquad (6)$$

which is a Fourier-component of electron density of a surface atom. We assume further that the wave vector k_0 in the initial state of electron is directed normally to the surface and along the z-axis.

In the calculations of the atom-surface interaction potential, the Morse potential is generally used, which has a shape typical of this interaction.[14] It is known[12] that the wave function of the ground bound state for this potential decreases as $\exp(-\hbar^{-1}(2MA)^{1/2}z)$ from the position of the potential well minimum at $z>a^{-1}$, where A and a are the parameters of the potential. A wave function with the same spatial damping was used in Ref. 15, where adsorption of atomic particles from gaseous phase by a surface was studied. We present the wave function of a particle in the $|\lambda_0\rangle$ state in the form

$$|\lambda_0\rangle=\pi^{-1/2}\varkappa^{3/2}\exp(-\varkappa R),\quad \varkappa=\hbar^{-1}(2M\varepsilon_b)^{1/2}. \qquad (7)$$

If the condition

$$\frac{k_0}{\varkappa}=\left(\frac{m}{M}\right)^{1/2}\left(\frac{\varepsilon_{k0}}{\varepsilon_b}\right)^{1/2}\ll 1, \qquad (8)$$

is satisfied, we can make the substitution $\exp(i\Delta\mathbf{k}\mathbf{R})\to i\Delta\mathbf{k}\mathbf{R}$ in (5)

With allowance for (7), the transition matrix element in the right side of (5) can be calculated in the region of radius of the order of $R\simeq\varkappa^{-1}$ near the potential well minimum. As is easy to estimate from (7), a typical value of $\varkappa^{-1}$ is $\simeq 10^{-2}$ Å. In this spatial domain, parabolic variation of the potential well may be neglected in the Schrödinger equation for $|\mathbf{g}n\rangle$. Taking it into account that ε_b is much greater than the energy of zero-order vibrations of a particle, and allowing for selection rules for dipole transitions with (8) satisfied, we get an expression for the wave function in the final state $|\mathbf{g}n\rangle$:

$$|\mathbf{g}n\rangle=2^{1/2}\Omega_i^{-1/2}\chi(g)\sin[g_{*z}R_z+\delta_n(\mathbf{g})]J_n(g_{*\rho}R_\rho)$$
$$\times\exp[in(\varphi_R-\varphi_{g_*})], \qquad (9)$$

where $n=0,\pm 1$;

$$g_*^2=g_{*z}^2+g_{*\rho}^2=2\hbar^{-2}M(\varepsilon_b+\varepsilon_g);$$

$g_{*z}>0$; J_n is a Bessel function. The function $\chi(\mathbf{g})$, the phase shift $\delta_n(\mathbf{g})$, and the polar angle $\varphi_{g*}(\mathbf{g})$ are specified by the shape of potential energy and depend on particle wave vector $\mathbf{g}$ at large distances from the surface. The factor $(2/\Omega_i)^{1/2}$ is related to normalization of the wave function in continuum. In the one-dimensional case in the quasi-classical approximation, we get a rough estimate for the function $\chi(\mathbf{g})$:

$$x(\mathbf{g})=(\varepsilon_g/(\varepsilon_g+\varepsilon_b)^{1/4}.$$

Formula (9) is conveniently expanded in spherical functions $Y_{1n}(\theta_R,\varphi_R)$ to yield:[16]

$$|\mathbf{g}n\rangle=(2/\Omega_i)^{1/2}\chi(\mathbf{g})G_n(g_*R)^{-1/2}J_{3/2}(g_*R)Y_{1n}(\theta_R,\varphi_R), \tag{10}$$

where

$$G_n=-6^{1/2}\pi[(1-n^2)i\cos\delta_n(\mathbf{g})\cos\delta_*(\mathbf{g}) +2^{-1/2}n\sin\delta_n(g)\sin\delta_*(g)\exp(-in\varphi_{g_*}(\mathbf{g}))]. \tag{11}$$

Here,

$$\cos\delta_*(\mathbf{g})=g_{*z}/g_*;\quad 0\leqslant\delta_*(\mathbf{g})\leqslant\pi/2;\quad 0\leqslant\varphi_{g*}(\mathbf{g})\leqslant 2\pi.$$

Taking (8) and (11) into account and substituting (7) and (10) in (5), the matrix element is readily calculated:

$$V_{ei}(\mathbf{k},\mathbf{k}_0;\mathbf{g}n,\lambda_0)=\frac{2^{23/4}\pi^{1/2}}{3^{1/2}}\cdot\frac{e^2\hbar^{5/2}\varepsilon_b^{5/4}(\varepsilon_b+\varepsilon_g)^{1/2}}{\Omega_e\Omega_i^{1/2}M^{5/4}(2\varepsilon_b+\varepsilon_g)^3}\chi(\mathbf{g})G_n^*\times\frac{Z-Q(\Delta k)}{\Delta k^2}[(1-n^2)(k\cos\theta_k-k_0)+2^{-1/2}nk\sin\theta_k\times\exp(-in\varphi_k)]. \tag{12}$$

Substituting (12) in (14) and performing summation over $\mathbf{k}$ and n, we get an expression for the differential cross section of the bound-free transition:

$$\frac{\partial\sigma_t}{\partial\varepsilon_g\partial O_g}=\frac{2^8}{\pi}\frac{Z^2e^4\varepsilon_b^{5/2}}{\varepsilon_{k0}}\frac{m}{M}\frac{\varepsilon_g^{1/2}(\varepsilon_b+\varepsilon_g)}{(2\varepsilon_b+\varepsilon_g)^6}[1-(\varepsilon_b+\varepsilon_g)/\varepsilon_{k0}]^{1/2}|\chi(\mathbf{g})|^2\times\left[P_0\cos^2\delta_0(g)\cos^2\delta_*(\mathbf{g})+\frac{1}{2}P_1\sin^2\delta_1(\mathbf{g})\sin^2\delta_*(\mathbf{g})\right]. \tag{13}$$

We introduced here, the dimensionless functions

$$P_0(Z,\varepsilon_{k0},\varepsilon_b+\varepsilon_g)=\int_{-1}^{1}dx\frac{(1-\zeta x)^2}{(1+\zeta^2-2\zeta x)^2}\times[1-Z^{-1}Q(k_0(1+\zeta^2-2\zeta x)^{1/2})]^2 \tag{14}$$

and

$$P_1(Z,\varepsilon_{k0},\varepsilon_b+\varepsilon_g)=\int_{-1}^{1}dx\frac{\zeta^2(1-x^2)}{(1+\zeta^2-2\zeta x)^2}\times[1-Z^{-1}Q(k_0(1+\zeta^2-2\zeta x)^{1/2})]^2, \tag{15}$$

where $x=\cos\theta_k=k_z/k$, $\zeta=[1-(\varepsilon_b+\varepsilon_g)/\varepsilon_{k0}]^{1/2}$.

The first term in the square brackets in the integral with respect to x in (14) and (15) determines the cross section of the bound-free transition (13) for the case of inelastic electron scattering by the nucleus of a surface atom with charge Z. The second term, $Z^{-1}Q$, stems from screening, by atomic electrons of the interaction potential of an incident electron and a particle nucleus. Both of these terms determine effective charge of a surface atom in inelastic scattering of an electron of energy ε_{k0}. For the energies $\varepsilon_b<\varepsilon_{k0}\leqslant\hbar^2/2ma_0$, where a_0 is of the order of atomic, the interaction potential of an incident electron and a surface atom with a nuclear charge Z is efficiently screened by the atomic electrons. At $\varepsilon_{k0}\geqslant\varepsilon_a$, a substantial increase in the transition cross-section may be expected due to decrease in the contribution of the atomic form-factor (6) to (14) and (15). For the electron energies $\varepsilon_{k0}\gg\varepsilon_a$, $Q(\Delta\mathbf{k})$ may be neglected in comparison with the nuclear charge Z,[12] and upon reaching its maximum, the transition cross section will decrease as $\sigma_t\sim\varepsilon_{k0}^{-1}$ according to (13).

Expressions (13)–(15) determine the particle distributions over energies ε_g and angles O_g in the continuum, up to the first order in the interaction operator for the transition amplitude. The particle distribution over solid angle O_g is determined by the dependences of the phase shift $\delta_n(\mathbf{g})$ and the functions $\delta_*(\mathbf{g})$ and $\chi(\mathbf{g})$ on the wave vector $\mathbf{g}$. These functions depend on the shape of potential energy. Experimental data on the particle angular distribution at large distances from the surface usually give a lobed structure.[1]

2.3. Numerical estimates

Let us consider collisions with fast electrons, $k_0a_0\gg 1$, where a_0 is of the order of atomic size. The major contribution to integrals (14) and (15) is given by inelastic large-angle $[\theta_k\gg(k_0a_0)^{-1}]$ scattering of electrons. In this case the atomic form-factor $Q(\Delta\mathbf{k})$ may be neglected in comparison with Z.[12] Light elements are implied here, since typical values of the electron energy are $\varepsilon_0=0.1$–10 keV. After integration over the solid angle O_g we get for the differential cross section:

$$\frac{\partial\sigma_t}{\partial\varepsilon_g}=\xi(\varepsilon_g)2^9\frac{Z^2e^4\varepsilon_b^{5/2}}{\varepsilon_{k0}}\frac{m}{M}\frac{\varepsilon_g^{1/2}(\varepsilon_b+\varepsilon_g)}{(2\varepsilon_b+\varepsilon_g)^6}, \tag{16}$$

where

$$\xi(\varepsilon_g)=(2\pi)^{-1}\int dO_g|\chi(\mathbf{g})|^2[P_0\cos^2\delta_0(\mathbf{g})\cos^2\delta_*(\mathbf{g})$$

$$+P_1 \sin^2 \delta_1(\mathbf{g}) \sin^2 \delta_*(\mathbf{g})]. \qquad (17)$$

In (16), $\xi(\varepsilon_g)$ is determined by potential energy near the surface and may depend on the particle energy in the continuum. According to (14)–(17), $\xi(\varepsilon_g)$ is a positive quantity bounded from above by a constant of the order of unity. For estimates, we shall assume below ξ to be a constant parameter.

According to (16), the distribution of desorbed particles over energy ε_g is a narrow peak. In the region of small energies, $\varepsilon_g \ll \varepsilon_0$, the differential cross section grows as $\varepsilon_g^{1/2}$. In the region of large energies, $\varepsilon_g \gg \varepsilon_0$, the cross section decreases as $\varepsilon_g^{-9/2}$. For the particle energy corresponding to the maximum differential cross section we get $\varepsilon_g^p \simeq 0.27\varepsilon_b$.

Upon integrating over the energy ε_g, we have from (16) for the transition cross section:

$$\sigma_t = \frac{13\pi}{2^{3/2}} \xi \frac{m}{M} \frac{Z^2 Ry^2}{\varepsilon_{k0}\varepsilon_b} a_B^2, \qquad (18)$$

where a_B is the Bohr radius.

Electron-beam-induced desorption of oxygen atoms from the (110) surface of a wide-gap semiconductor SnO_2 was studied in Ref. 17. It was found that at an energy $\varepsilon_{k0}=160$ eV the desorption cross-section was $\sigma \simeq 2.8 \cdot 10^{-20}$ cm^2 and remained constant until stoichiometry of the SnO surface was achieved. Oxygen desorption from the (110) surface of TiO_2 was examined in Ref. 18. The cross section $\sigma \simeq 0.3 \cdot 10^{-20}$ cm^2 was obtained at an electron energy $\varepsilon_{k0}=160$ eV. This value agrees with the results of Ref. 19 on desorption of O atoms previously chemisorbed on the (100) surface of W. For the β_2-phase of oxygen, with submonolayer coating of the surface by an adsorbate, the desorption cross section was $\sigma=(1.4\pm0.5)\cdot 10^{-21}$ cm^2 at $\varepsilon_{k0}=150$ eV. In these works, the data were qualitatively explained on the basis of a mechanism proposed in Ref. 7. Desorption was assumed to result from ionization of the core levels of surface atoms with subsequent interatomic Auger relaxation.[2] It was believed that the interatomic Auger process may be accompanied by removal of three electrons from an oxygen ion O^{2-} thus imparting positive charge to it and resulting in Coulomb repulsion of the particles.[1,2]

To estimate the cross-sections of desorption due to the channel of bound-free transitions of surface atoms, we can use formula (18) for the transition cross section. The reason is that the energy relaxation time for an atomic particle is of the order of 0.1 ps,[4] which is at least comparable with the time of particle motion in a potential field near the surface.[1,4,8] For an ^{16}O atom and $\varepsilon_{k0}=1$ keV, $\varepsilon_b=4$ eV (Ref. 20) and, $\xi=0.25$, we obtain from (18) the estimate $\sigma_t=10^{-20}$ cm^2. This agrees well with the experimental data given above.[17–19] In this case, $k_0\varkappa \simeq).3$.

3. PHOTOEFFECT FOR SURFACE IONS

3.1. Phototransition amplitude

The Hamiltonian for surface ions interacting with an incident electromagnetic wave may be represented in the form

$$H=\sum_\lambda \varepsilon_\lambda c_\lambda^+ c_\lambda + H_{\rm rad} - \int dR \frac{q}{cM} \psi^+ A p \psi + \int dR \frac{q^2}{2c^2 M} A^2 \psi^+ \psi. \qquad (19)$$

The first term here is the unperturbed energy of the ions. As before, the states $|\lambda\rangle$ include both bound states at the surface and continuum states. The second term, $H_{\rm rad}$, is the unperturbed energy of electromagnetic field. Two last terms in (19) are the operators of interaction between a bound ion and electromagnetic field. q and M are respectively the charge and the mass of a particle; $\mathbf{p}=-i\hbar\nabla_R$ is the particle momentum operator; $\mathbf{A}$ is the operator of vector potential of electromagnetic field, and $\psi=\Sigma_\lambda c_\lambda |\lambda\rangle$.

In the initial state $|\lambda_0\rangle$, a particle is in the ground state in a deep potential well near the surface. The final state corresponds to a continuum state for a free particle $|\mathbf{g}n\rangle$.

The amplitude of a bound-free transition $B(\mathbf{g}n;\lambda_0)$ is connected with the S-matrix, defined by (19) in the interaction representation, by Eq. (3), where

$$E_i=-\varepsilon_b+\varepsilon_i; \quad E_f=\varepsilon_{gn}+\varepsilon_f;$$

ε_b in the binding energy of the particle in the $|\lambda_0\rangle$ state; ε_{gn} is the particle energy in the continuum state $|\mathbf{g}n\rangle$; ε_i and ε_f are the energies of electromagnetic field in the initial $|i\rangle$ and the final $|f\rangle$ states, respectively.

Eqs. (3) and (19) can be utilized to investigate the photoeffect for surface ions in the case of multiphoton absorption by a bound particle. We restrict ourselves below to the case of a single-photon process. This suggests that the photon energy $\hbar\omega$ is greater than ε_b.

3.2. The cross section of a single-photon bound-free transition

Let us consider a linearly polarized electromagnetic wave with the polarization vector $\mathbf{s}$ lying in the zx-plane and the angle of incidence θ_0 measured from the z-axis which coincides with the external normal to the surface. The x- and y-axes are parallel to the surface.

From (3) and (19), the differential cross section of the transition in the dipole approximation has the form

$$\frac{\partial \sigma_t}{\partial O_g} = (2\pi)^{-1} \alpha \frac{q^2}{e^2} \frac{\hbar\Omega_i}{M^2\omega} \sum_n \int dg g^2 |\langle \mathbf{g}n|sp|\lambda_0\rangle|^2 \times (\varepsilon_{gn}+\varepsilon_b-\hbar\omega). \qquad (20)$$

Here α is the fine-structure constant.

The matrix element of the transition in (20) is easily calculated using (7) and (10):

$$\langle \mathbf{g}n|sp|\lambda_0\rangle = \Omega_i^{-1/2}\frac{2^{9/4}}{3^{1/2}}\pi^{-1/2}\frac{\hbar^{3/2}\varepsilon_b^{5/4}(\varepsilon_b+\varepsilon_g)^{1/2}}{M^{1/4}(2\varepsilon_b+\varepsilon_g)^2}\chi(g)G_n^*$$
$$\times[(1-n^2)\sin\theta_0 - 2^{-1/2}n\cos\theta_0)]. \quad (21)$$

Substituting (21) to (20), using $\varepsilon_g=\hbar^2g^2/2M$, and summing over $\mathbf{g}$ and n, we finally get an expression for the differential cross section:

$$\frac{\partial\sigma_t}{\partial O_g}=2^6\alpha\frac{q^2}{e^2}\frac{\hbar^2\varepsilon_b^{5/2}}{M}\frac{(\hbar\omega-\varepsilon_b)^{1/2}}{(\hbar\omega+\varepsilon_b)^4}F(\mathbf{g},\theta_0), \quad (22)$$

where

$$F(\mathbf{g},\theta_0)=|\chi|^2(\cos^2\delta_0\cos^2\delta_*\sin^2\theta_0$$
$$+\tfrac{1}{2}\sin^2\delta_1\sin^2\delta_*\cos^2\theta_0). \quad (23)$$

The function $F(\mathbf{g},\theta_0)$ specifies the angular distribution of photoexcited particles for arbitrary incidence angle of radiation.

3.3. Numerical estimates

Let us introduce the quantity

$$\xi(\varepsilon_g,\theta_0)=(2\pi)^{-1}\int dO_g F(g,\theta_0).$$

Its value depends essentially on form of potential energy and may be a function of the particle energy in the continuum. According to (23), $\xi(\varepsilon_g)$ is a positive quantity bounded from above by a constant of the order of unity. To make further estimates, we consider ξ as a constant parameter independent of ε_g. Upon integration over the angle O_g, we get from (22) and (23)

$$\sigma_t(\hbar\omega)=\zeta\pi 2^7\alpha\frac{q^2}{e^2}\frac{\hbar^2\varepsilon_b^{5/2}}{M}\frac{(\hbar\omega-\varepsilon_b)^{1/2}}{(\hbar\omega+\varepsilon_b)^4}. \quad (24)$$

According to (24), the phototransition cross-section is a narrow peak as a function of photon energy. The maximum cross-section value:

$$\sigma_t=\xi(\theta_0)\frac{7^{7/2}\pi\alpha}{2^{17/2}}\frac{q^2}{e^2}\frac{\hbar^2}{M\varepsilon_b} \quad (25)$$

corresponds to the energy $\hbar\omega=(9/7)\varepsilon_b$. In this case, the kinetic energy of photoexcited particles is $\varepsilon_g=(2/7)\varepsilon_b$. Near the threshold of the process, at the photon energy $\hbar\omega=\varepsilon_b$, the cross section grows as $(\hbar\omega-\varepsilon_b)^{1/2}$ with $\hbar\omega$. For large energies, $\hbar\omega\gg\varepsilon_b$, the cross section decreases as $(\hbar\omega)^{-7/2}$.

The experimental data on laser-induced desorption of atomic particles from polar dielectric surfaces have recently been reviewed in Ref. 21. The absolute yield of the particles was not found in many cases.

Photodesorption of Ga atoms from the $(\bar{1}\bar{1}\bar{1})$ surface of GaP was studied in Ref. 22. The photon energy, $\hbar\omega=2.14$ eV, was less than the band gap for indirect transitions. It was found that the Ga atom detection limit in the installation used corresponded to desorption of $\eta\simeq 10^{-5}$ of Ga surface atoms by a single laser pulse at a fluence $E_{th}\simeq 0.1$ J/cm^2. We can estimate the desorption cross section from these data as

$$\sigma=\eta\hbar\omega/E_{th}\simeq 0.4\cdot 10^{-22}\ \text{cm}^2.$$

Since the photon energy was less than the bandgap, it was assumed in Refs. 22,23 that photodesorption results from electron transitions via surface states of the semiconductor. Feasibility of localization of an additional hole at a surface Ga^+ ion was discussed qualitatively. Such localization may result in breaking of a particle-surface bond and further in desorption of an atomic particle.

According to Ref. 23, there are several types of sites for Ga atoms at GaP surface. At $\hbar\omega=2.14$ eV, desorption via the channel of single-photon bound-free transitions may occur from the following sites: Ga adatom ($\varepsilon_b\simeq 1.70$ eV), P vacancy ($\varepsilon_b\simeq 1.46$ eV), Ga-P vacancy ($\varepsilon_b\simeq 1.32$ eV), and P(Ga) site ($\varepsilon_b\simeq 0.44$ eV).[23] We estimate the transition cross-section for "Ga-adatom" sites, where Ga^+ ions with a charge $+1e$ are localized.[23] From (24) we get for $\varepsilon_b=1.7$ eV, $\hbar\omega=2.14$ eV, $q=+1e$, and $\zeta=0.2$:

$$\sigma_t=0.6\cdot 10^{-22}\ \text{cm}^2,$$

in good agreement with the cited value obtained from the experimental data on photodesorption from the $(\bar{1}\bar{1}\bar{1})$ surface of GaP.

It should be noted that although the charge of a Ga adsorbed atom is $+1e$ at the surface, the electron ground state of the system Ga adsorbed atom-GaP $(\bar{1}\bar{1}\bar{1})$, which determines the potential energy of a photoexcited particle, should correspond to a neutral state $Ga^0+[GaP(\bar{1}\bar{1}\bar{1})]^0$ at large distances from the surface. The reason is that the ionization potential of Ga atoms, 6.0 eV, is much greater than the work function for the $(\bar{1}\bar{1}\bar{1})$ surface of GaP, 3.2 eV. Thus, neutral Ga atoms are ultimately desorbed from the surface.

4. CONCLUSION

We have investigated a channel of interaction between surface atoms and incident radiation accompanied by particle transition from a bound state in a deep potential well to continuum. This channel does not require initial electron excitations in the system under the action of radiation, and is possible owing to the presence of a bond between an atomic particle and a surface.

It was found that bound-free transitions of surface atoms result in a certain distribution of particle energy ε_g in continuum corresponding to the ground electron state of the system. If the atomic ionization potential I exceeds the work function Φ, then desorption of only neutral atoms in the ground or excited electron states is possible for the particle energies $0<\varepsilon_g<I-\Phi$. The particle energies $\varepsilon_g>I-\Phi$ fall within the continuum regions for both ground and excited ionic and neutral electron states of the particle+surface system.[1,2] In this case, electron transitions in the system are allowed and are accompanied by desorption of ions with kinetic energies smaller than those of neutral atoms. It should be noted, however, that at large energies, $\varepsilon_g\gg\varepsilon_b$, the differential cross section of a bound-free transition decreases (as $\varepsilon_g^{-9/2}$ for an electron beam, for instance). This explains why neutral particles are prefer-

entially desorbed if the work function for the surface is smaller than the atomic ionization potential.

The investigated interaction channel exists also for bound ions in crystal lattice of semiconductors in a field of an electromagnetic wave.[24] In this case photon absorption by a bound intrinsic or impurity ion may induce an above-barrier transition of a particle from a site or an interstitial site to its band of Bloch states in the crystal lattice. A photoexcited particle can efficiently migrate in a crystal, in particular, towards a semiconductor surface, thus making a contribution to photodesorption. However, its interaction with phonons or electrons in the crystal returns the particle to a bound state. This process leads to photoinduced generation and diffusion of defect ions in semiconductors.

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[1] *Desorption Induced by Electronic Transitions*, Eds. G. Betz and P. Varga, Springer-Verlag, Berlin, New York (1990).
[2] V. N. Ageev, O. P. Burmistrova, and Yu. A. Kuznetsov, Usp. Fiz. Nauk **158**, 389 (1989) [Sov. Phys. Usp. **32**, 588 (1989)].
[3] M. A. Schildbach and A. V. Hamza, Phys. Rev. B **45**, 9878 (1992).
[4] J. C. Tully, in *Desorption Induced by Electronic Transitions*, Eds. N. H. Tolk, M. M. Traum, J. C. Tully, and T. E. Madey, Springer-Verlag, Berlin, New York, p. 31 (1983).
[5] D. Menzel and R. Gomer, J. Chem. Phys. **41**, 3311 (1964).
[6] P. A. Redhead, Can J. Phys. **47**, 886 (1964).
[7] M. L. Knotek and P. J. Feibelman, Phys. Rev. Lett. **40**, 964 (1978).
[8] B. Hellsing, Surf. Sci. **282**, 216 (1993).
[9] P. Nordlander and J. C. Tully, Phys. Rev. B **42**, 5564 (1991).
[10] S. Gao and B. I. Lundqvist, Prog. Theor. Phys. Suppl. no. 106, 405 (1991).
[11] N. Itoh, Phys. Lett. A **108**, 480 (1985).
[12] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics, Nonrelativistic Theory*, Pergamon (1977)
[13] T. Y. Wu and T. Omura, *Quantum Theory of Scattering*, Prentice-Hall Inc., N.Y. (1962).
[14] B. M. Rice, L. M. Raff, and D. L. Thompson, Surf. Sci. **198**, 360 (1988).
[15] T. B. Grimley, Chem. Phys. Lett. **177**, 129 (1991).
[16] G. N. Watson, *A Treatise on the Theory of Bessel Functions*, 2-d ed. repr., Univ. Press, Cambridge, Macmillan, New York (1945).
[17] R. G. Egdell, S. Eriksen, and W. R. Flavell, Surf. Sci. **192**, 265 (1987).
[18] R. G. Egdell, S. Eriksen, and W. R. Flavell, Surf. Sci. **180**, 263 (1986).
[19] S. W. Ballard and E. M. Williams, Surf. Sci. **80**, 450 (1979).
[20] C. Kohrt and R. J. Gomer, J. Chem. Phys. **52**, 3283 (1980).
[21] N. Itoh, Nucl. Instr. and Meth. B **27**, 155 (1987).
[22] K. Hattory, Y. Nakai, and N. Itoh, Surf. Sci. **227**, L115 (1990).
[23] C. K. Ong, G. S. Khoo, K. Hattory, Y. Nakai, and N. Itoh, Surf. Sci. **259**, L787 (1991).
[24] A. I. Agafonov, Physica B, **191**, 355 (1993).

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