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## Surface Science

journal homepage: [www.elsevier.com/locate/susc](http://www.elsevier.com/locate/susc)

# Effects of electron levels broadening and electron temperature in tunnel structures based on metal nanoclusters

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## ARTICLE INFO

## Article history:

Received 4 September 2009

Accepted for publication 9 November 2009

Available online 18 November 2009

## Keywords:

Electron density

Excitation spectra calculations

Equilibrium thermodynamics and statistical mechanics

Semi-empirical models and model calculations

Tunneling

## ABSTRACT

We study the influence of energy levels broadening and electron subsystem overheating in island electrode (cluster) on current–voltage characteristics of three-electrode structure. A calculation scheme for broadening effect in one-dimensional case is suggested. Estimation of broadening is performed for electron levels in disc-like and spherical gold clusters. Within the two-temperature model of metallic cluster and by using a size dependence of the Debye frequency the effective electron temperature as a function of bias voltage is found approximately. For helium temperature of ion subsystem, the heating temperature of electrons in a quantum disc is almost one order of magnitude higher than that in a sphere; it achieves thousands of Kelvin. We suggest that the effects of broadening and electron overheating are responsible for the smoothing of current–voltage curves, which is observed experimentally at low temperatures in structures based on clusters consisting of accountable number of atoms. However, a role of the broadening is much more significant.

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## 1. Introduction

The ultradispersed metallic systems are prospective objects of nanotechnology. Therefore understanding of their physical properties is of scientific and hopefully of practical interest.

Transport of electrical charge across a nanoscale tunnel junction is accompanied by many effects, such as the Coulomb blockade of the average current, transfer of energy between electrons and ions, and consequently heating of the junction. In nanometer scale devices electron transport can occur through well-resolved quantum states. If the temperature is increased, the Coulomb and quantum staircases of current are gradually smeared out by thermal fluctuations (see, for example [1,2]).

Simple tunnel construction can be schematically represented by the distinctive ‘sandwich’ [3–6]: Au(111) thick film/dielectric nanofilm/isolated Au cluster/vacuum gap/polycrystalline Au (a tip of STM). The monoatomic disc-shaped [3,4] or spherical-like [5,6] gold clusters self-organize on the dielectric layer.

Some of the experimental features of the  $I$ – $V$  curves were investigated in Ref. [7] including the current gap in the low temperature limit [8]. However, the fact of smoothing of staircases for granule–molecule at low temperatures is still not understood [1–6]. Such a smoothing is typical for molecular transistors. Moreover, the observed width of current gap decreases significantly as temperature increases from 5 K to 300 K in structure based on

disc-shaped cluster with the radius  $\sim 2$  nm [3]. However, for spherical granules, of radius  $\sim 1$  nm, a similar dependence of current gap cannot be traced back by a comparison of gaps at  $T = 30$  [5] and 300 K [6].

Such ‘anomaly’ of the temperature dependence in the regime of the Coulomb blockade and strong quantization can hardly be explained within the concept of a quasi-equilibrium electronic gas and resonance tunneling through the stationary electronic states [9–11].

The aim of this paper is to analyze two mechanisms: (i) the broadening of electronic levels due a tunnel effect, (ii) electronic gas heating in the isolated metallic clusters of disc-like and spherical shape in presence of bias voltage. Absence of clear steps of the Coulomb and quantum staircases on the experimental current–voltage curves of single-electronic devices at the low temperatures is explained by these effects.

In the typical electronic circuit the current flow leads to the non-equilibrium regime of interaction between electron and the phonon (ion) subsystems. Dynamics of a relaxation of non-equilibrium electrons was examined in metals [12–14], continuum films [15,16], nanowires [17–21], granular films [16,22–26], free clusters [27,28], including the regime under the action of the pico- and femtosecond laser pulses [16,29–31]. Very few papers deal with the direct experiments with the free metal clusters within ultra-short pulse duration (see [32,33] and references therein). Kinetics of the relaxation between electrons and lattice can be traced within the pump–probe scheme, where the pump and probe pulses are both very short in duration with respect to the characteristic time

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scale of the process, and the delay between the two pulses is varied.

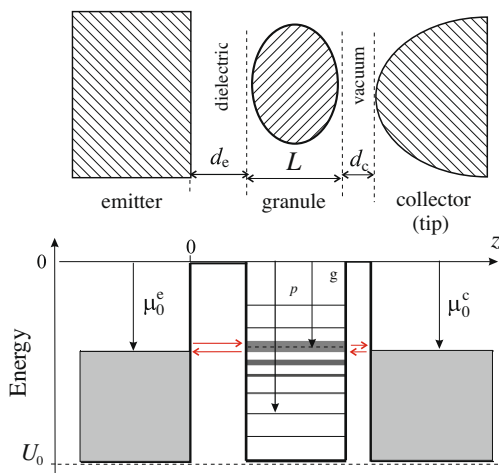
Predicted earlier size dependence of the Debye temperature [34] is experimentally confirmed in Ref. [35] and it is determined precisely by temperature-dependent study in Ref. [36]. Suppression of the electron–phonon interactions in granules is a result of deformations of a phonon spectrum in these systems. This interaction can be suppressed so that electron–electron interaction appears as a basic mechanism of dissipation affecting a particle energy. This leads to the overheating of electronic subsystem which can be described by Fermi statistics with some effective (raised) temperature while the ionic subsystem temperature varies only slightly. It is supposed that the relaxation of the non-equilibrium electrons in small metal particles, films [22–25] and wires [37,38] occurs due to excitation of the Rayleigh waves or surface acoustic phonons.

According to the Weyl's theorem (see Ref. [39]), it is possible to separate the bulk and surface acoustical phonons only for the large metal sample. For small-sized samples the modes are mixed, a sound velocity becomes indefinite and, as a rule, in practice it is used as a fitting parameter. On the other hand, measurements of an electron–ion power exchange in the free clusters  $\text{Na}_{16-250}^+$  [33] have demonstrated that, for reasonable estimations, it is quite possible to use the concept of bulk phonons, but with the account of the size dependence of the Debye frequency. Such an approach for the metallic nanoclusters, films and wires can be considered as an extrapolation.

## 2. Broadening of levels

The scattering matrix relates the initial state and the final state for an interaction of particles. The free electronic states of the cluster do not decay so they are stationary. For free clusters the poles of the scattering matrix  $S(k)$ , located on the real axis at the plane of complex values of waving numbers  $k$ , correspond to the stationary states.

If a cluster is placed between electrodes, its electronic states become quasi-stationary. Broadening occurs due to a tunneling effect by analogy with the formation of energy bands in a crystal. The broadening increases with the increase of the bias voltage applied between electrodes. Both tunnel barriers are three-dimensional. Therefore, the problem of calculation of broadening, in general case, is far from being trivial. An analytical solution of resonance



**Fig. 1.** The energy diagram for tunnel structure based on the non-magic granule (sphere or disc) before application of voltage.  $L = 2R$  and  $H$  for spherical clusters with a diameter  $2R$  and a disc with thickness  $H$ , accordingly.

tunneling problem is possible only for one-dimensional geometry and rectangular barriers (see [40]).

According to the uncertainty principle broadening effects are related to the finite life time. Self-energies of the quasi-stationary states become complex and their imaginary parts describe levels broadening. The poles of the  $S$ -matrix corresponding to these states are located in the lower half of the complex plane wave number  $k$ . The state with well defined energy is accordingly replaced by the Lorentz distribution with the scale parameter which specifies the half-width at half-maximum  $\gamma_p$ :

$$L_p(\varepsilon) = \frac{1}{2\pi} \frac{\gamma_p}{(\varepsilon - \varepsilon_p)^2 + \gamma_p^2/4}. \quad (1)$$

Here an index  $p$  denotes the set of quantum numbers (except for a spin) which correspond to the single-electron state with energy  $\varepsilon_p$  (Fig. 1).  $L_p(\varepsilon) \rightarrow \delta(\varepsilon - \varepsilon_p)$  as  $\gamma_p \rightarrow 0$  where  $\delta(x)$  is the Dirac  $\delta$ -function.

Taking into account the broadening function, the electron density of states can be expressed as

$$\bar{\rho}(\varepsilon) = 2 \sum_p L_p(\varepsilon), \quad (2)$$

where the factor 2 takes into account a spin degeneracy.

Current flowing through a quantum granule (with limitation on its Coulomb instability [7]) is determined by the equality condition between the emitter and collector currents ( $I^e = I^c \equiv I$ ) or

$$-e \sum_{n_{\min}}^{n_{\max}} P_n (\bar{w}_n^e - \bar{w}_n^c) = -e \sum_{n_{\min}}^{n_{\max}} P_n (\bar{w}_n^c - \bar{w}_n^e). \quad (3)$$

The probability  $P_n$  of finding of  $n$  'surplus' ( $n > 0$ ) or 'failing' ( $n < 0$ ) electrons at central electrode is defined by the master equation in the stationary limit. In reality, one calculates the reduced current  $\tilde{I} \equiv I/(eP_0I^e)$  where  $I^{e,c}$  are tunnel rates, i.e. probabilities (contact transparencies) per unit time, ( $-e$ ) is the electron charge. In order to find  $P_{n \neq 0}/P_0$  the recurrent relation is used:

$$P_{n+1} = P_n \frac{w_n^{\text{in}}}{w_{n+1}^{\text{out}}}, \quad (4)$$

where  $w_n^{\text{in}} = \bar{w}_n^e + \bar{w}_n^c$  and  $w_n^{\text{out}} = \bar{w}_n^e + \bar{w}_n^c$  are the total electron streams from/to leads into/out the cluster, and  $\bar{w}_n^{e,c}$  are the partial tunneling streams, accordingly. Here the upper/lower arrows and indexes 'e, c' denote the emitter-granule and collector-granule and back transitions in accordance with arrows direction.

Taking into account the broadening of levels for  $V > 0$ , we have

$$\bar{w}_n^e = \frac{1}{\pi} \Gamma^e \sum_p \int_{U_0 + U^e}^{+\infty} \frac{\gamma(\varepsilon^e)}{(\varepsilon' - \varepsilon^e)^2 + (\gamma(\varepsilon^e)/2)^2} \times f(\varepsilon' - \mu_V^e; T) \left[ 1 - f(\varepsilon' - \mu_C^e; T_e) \right] d\varepsilon', \quad (5)$$

$$\bar{w}_n^c = \frac{1}{\pi} \Gamma^c \sum_p \int_{U_0 + U^c}^{+\infty} \frac{\gamma(\varepsilon^c)}{(\varepsilon' - \varepsilon^c)^2 + (\gamma(\varepsilon^c)/2)^2} \times f(\varepsilon' - \mu_V^c; T) \left[ 1 - f(\varepsilon' - \mu_C^c; T_e) \right] d\varepsilon', \quad (6)$$

$$\bar{w}_n^e = \frac{1}{\pi} \Gamma^e \sum_p \int_{U_0 + U^e}^{+\infty} \frac{\gamma(\varepsilon^e)}{(\varepsilon' - \varepsilon^e)^2 + (\gamma(\varepsilon^e)/2)^2} \times [1 - f(\varepsilon' - \mu_V^e; T)] f(\varepsilon' - \mu_C^e; T_e) d\varepsilon', \quad (7)$$

$$\begin{aligned} \bar{w}_n^{\pm} = & \frac{1}{\pi} \Gamma^c \sum_p \int_{U_0 + \bar{U}^{\pm}}^{+\infty} \frac{\gamma(\bar{\varepsilon}^c)}{(\varepsilon' - \bar{\varepsilon}^c)^2 + (\gamma(\bar{\varepsilon}^c)/2)^2} \\ & \times [1 - f(\varepsilon' - \mu_V^c; T)] f(\varepsilon' - \mu_C^c; T_e) d\varepsilon', \end{aligned} \quad (8)$$

where  $f(\varepsilon - \mu; T) = \{1 + \exp[(\varepsilon - \mu)/k_B T]\}^{-1}$  is the Fermi–Dirac distribution. For the sake of simplicity, we neglect here the energy dependence of  $\Gamma^{e,c}$  [7].

Because of the applied voltage and charging of a granule [7], the spectrums and the chemical potentials are shifted:

$$\begin{aligned} \bar{\varepsilon}^e &= \varepsilon_p + \bar{E}_C(n \pm 1/2) - e\eta^+ V, \\ \bar{\varepsilon}^c &= \varepsilon_p + \bar{E}_C(n \mp 1/2) + e(1 - \eta^+) V, \\ \bar{U}^e &= -e\delta\phi + \bar{E}_C(n \mp 1/2) - e\eta^+ V, \\ \bar{U}^c &= -e\delta\phi + \bar{E}_C(n \pm 1/2) + e(1 - \eta^+) V, \\ -\mu_V^e &\equiv W_0^e, \quad \mu_C^{e,c} = \mu^g + \bar{U}^{e,c}, \quad \mu_V^c = \mu_0^c - eV. \end{aligned}$$

Here the upper/under arrows at the left correspond to the following signs at the right.  $\varepsilon_p$  is electron spectrum in a cluster in absence of both the voltage and charging;  $\bar{E}_C = e^2/C$  is the characteristic Coulomb energy of charging, where  $C$  is self-capacitance of a single granule in vacuum;  $W_0^e \equiv -\mu_0^e$  is a work function of semi-infinite metal;  $\mu^g$  is a electron chemical potential of granule;  $\delta\phi = (\mu^g - \mu_0^{e,c})$  is a contact potential difference between cluster and electrodes.

For  $V > 0$  the fraction of voltage reads

$$\eta^+ = \frac{d_e + \epsilon L/2}{\epsilon(d_c + L) + d_e}, \quad (9)$$

where  $L \equiv 2R$  and  $H$  for a sphere and disc, accordingly,  $\epsilon$  is a dielectric constant of film which covers the left electrode.  $\eta^+ V$  is the potential in a coordinate  $z = d_e + L/2$  in the case of absence of cluster (it is assumed that the electric field in the cluster is screened completely). For  $V < 0$  the voltage fraction  $\eta^-$  equals  $1 - \eta^+$ .

As an approximation, the profile of the one-electron effective potential in the cluster can be represented as a potential well of the depth  $U_0 < 0$  (particle-in-a-box model). The three-dimensional Schrödinger equation for a quantum box can be separated into one-dimensional equations. The spectrum of wave numbers in a spherical and cylindrical potential wells are determined from the continuity condition of a logarithmic derivative of the wave function on the boundaries.

Neglecting the area near cylinder edges, the energy spectrum in metal nanodisc is found by a simple way [7,8] as follows:

$$\varepsilon_p = U_0 + \frac{\hbar^2}{2m_e} (k_{n_z}^2 + k_{\perp}^2), \quad (10)$$

where  $U_0 < 0$  is the position of conductivity band of a semi-infinite metal,  $k_{\perp}$  is a solution of wave equation for radial direction. Quantization of the wave number  $k_{n_z}$  along the cylinder axis is determined by the solution of the equation:

$$k_{n_z} H = n_z \pi - 2 \arcsin(k_{n_z}/k_0), \quad (11)$$

where  $n_z$  is the integer number,  $\hbar k_0 \equiv \sqrt{2m_e|U_0|}$  [41]. Since the tunneling takes place mainly in  $z$ -direction, ‘partial’ broadening of  $k_{n_z}$  spectrum corresponds to general spectrum  $\varepsilon_p$ .

In order to calculate the electron levels broadening in quantum metal disc, let us consider the decay of cluster’s states due to the tunneling. For simplest potential profile which corresponds to Fig. 1, we use the solution of the Schrödinger equation in the form:

$$\bar{\psi}(z) = \begin{cases} e^{ik_{n_z} z} + B_1 e^{-ik_{n_z} z}, & z < 0, \\ A_1 e^{k_{n_z} z} + B_2 e^{-k_{n_z} z}, & 0 < z < d_e, \\ A_2 e^{ik_{n_z} z} + B_3 e^{-ik_{n_z} z}, & d_e < z < d_e + H, \\ A_3 e^{k_{n_z} z} + B_4 e^{-k_{n_z} z}, & d_e + H < z < d_e + H + d_c, \\ A_4 e^{ik_{n_z} z}, & z > d_e + H + d_c \end{cases} \quad (12)$$

for the electrons moving from the left to the right and

$$\bar{\psi}(z) = \begin{cases} e^{-ik_{n_z} z} + B_5 e^{ik_{n_z} z}, & z > d_e + H + d_c, \\ A_5 e^{-k_{n_z} z} + B_6 e^{k_{n_z} z}, & d_e + H < z < d_e + H + d_c, \\ A_6 e^{-ik_{n_z} z} + B_7 e^{ik_{n_z} z}, & d_e < z < d_e + H, \\ A_7 e^{-k_{n_z} z} + B_8 e^{k_{n_z} z}, & 0 < z < d_e, \\ A_8 e^{-ik_{n_z} z}, & z < 0 \end{cases} \quad (13)$$

for the stream falling from right to left, respectively. Here

$$\hbar k_{n_z} = \sqrt{2m_e|U_0| - \hbar^2 k_{n_z}^2}.$$

Using the continuity condition of the wave functions on the boundaries  $z = 0$ ,  $d_e$ ,  $d_e + H$  and  $d_e + H + d_c$  we obtain the system of equations for the determination of the coefficients  $A$  and  $B$  which we then solve numerically by the LU-expansion method.

A total wave function can be written using the  $S$ -matrix as

$$\bar{\psi}(z) \sim \{\bar{\psi}(z) - S\bar{\psi}(z)\}.$$

For any coordinates inside the electron reservoirs (left and right electrodes),  $z = z^* \leq 0$  or  $z^* \geq d_e + H + d_c$  ( $H = L$  for disc at Fig. 1), one can calculate the matrix

$$S = (\bar{\psi} / \bar{\psi})|_{z=z^*}. \quad (14)$$

By the Muller’s method we calculate the pole of  $S$ -matrix at the lower half-plane of the complex wave numbers  $k$ , in the vicinity of point  $k_{n_z}$ . The imaginary part of the energy  $\hbar^2 k_{n_z}^2 / 2m_e$  gives the energy broadening.

It is easy to generalize a method on  $V \neq 0$  regime. In this case underbarrier wave functions will be expressed through the Airy functions.

For estimation of the broadening in a spherical cluster, it is possible to use the solution of the well-known problem for open dot – spherically symmetric potential in depth  $U_0$ , of radius  $R$  and barrier thickness  $d_c$ . We define broadening by analogy with the book [40] as

$$\gamma_p \approx 8e^{-2\kappa_p d_c} \frac{\hbar^2 k_p^3 \kappa_p^3}{m_e k_0^4 (1 + \kappa_p d_c)} \quad (15)$$

for  $e^{-\kappa_p d_c} \ll 1$ .

### 3. Balance equation

The two-temperature model describes a system of electrons and ions, which is out of equilibrium between electronic and ionic subsystems. For a metallic sample, this condition can be fulfilled, provided one applies an electric field.

In a two-temperature model a balance equation in a cluster in presence of voltage has the simplest form

$$\Omega \frac{\partial(c_e T_e)}{\partial t} = \mathcal{P}(T_e, T_i) - Q(T_e, T_i), \quad (16)$$

$$\Omega \frac{\partial(c_i T_i)}{\partial t} = Q(T_e, T_i), \quad (17)$$

where  $c_{e,i}$  is specific heat capacity of electronic and ionic subsystems (with temperatures  $T_e$  and  $T_i$ , respectively) of cluster with the volume  $\Omega$ ,  $\mathcal{P}$  is a input power,  $Q$  is the exchange energy between electrons and ions per second.

Since the specific heat of the electronic subsystem is much smaller than that of phonons, the electron–electron and the phonon–phonon processes are much faster than the electron–phonon processes, i.e. the characteristic relaxation time for the electron subsystem temperature is much shorter than that for the phonon subsystem. The result is that when injecting power into the metal cluster, the electron temperature grows very rapidly until the energy flux from electrons to phonons becomes equal to the absorbed power so that the local equilibrium in the electron subsystem is achieved ( $dT_e/dt = 0$ ),

$$\mathcal{P}(T_e, T_i) - Q(T_e, T_i) = 0. \quad (18)$$

The injected power can be counted up by simple way in the form

$$\mathcal{P}^\pm = I^\pm \eta^\pm V^\pm, \quad (19)$$

using the experimental  $I(V)$  dependence.  $I/e$  is the electron stream, and the value  $e\eta V$  equals approximately the energy diapason for injected electrons ( $eV \ll W_0$ ). We assume the input power to be the one which is measured by the external apparatus (this is what is most likely in the straightforward experimental realization). The dissipation does not only take place in the cluster, but also in the contacts and in the electrodes. Then  $I(1 - \eta)V$  corresponds to the energy dissipation channels.

For  $Q$  we use the result of Ref. [13], derived for any temperatures of electrons and lattices of massive metals, on the basis of kinetic equation:

$$Q(T_e, T_i) = \Omega \frac{2}{(2\pi)^3} \frac{m_e^2 U_{e-ph}^2 k_B^5 T_{D0}^5}{h^7 \rho s^4} \times \left\{ \left( \frac{T_e}{T_{D0}} \right)^5 \int_0^{T_{D0}/T_e} \frac{x^4 dx}{e^x - 1} - \left( \frac{T_i}{T_{D0}} \right)^5 \int_0^{T_{D0}/T_i} \frac{x^4 dx}{e^x - 1} \right\}. \quad (20)$$

Here  $U_{e-ph}$  is the electron–phonon interaction constant,  $T_{D0}$  is the Debye temperature in a massive metal,  $\rho$  is the density of Au, and  $s$  is the ‘average’ sound speed.

For low-dimensional object of a volume  $\Omega$  and surface area  $S$  the size dependence of the Debye temperature in quasi-classical approximation is given by [34]:

$$T_D = T_{D0} \frac{1 + \pi\xi/8}{1 + \pi\xi/4 + (\xi/3)^2}, \quad \xi = \frac{1}{k_{WS}} \frac{S}{\Omega} \quad (21)$$

where  $k_{WS} = (6\pi^2/v)^{1/3}$  is the maximum wave number in a massive metal,  $v = 4\pi r_0^3/3$ , and  $r_0$  is the atom density parameter ( $r_0 = 0.156$  nm for Au).

After that, the expression (20), in which a replacement  $T_{D0} \rightarrow T_D$  (21) is performed, is substituted in (18). Under the assumption of the equality between the temperatures of the ionic subsystem  $T_i$  (constant throughout the tunnel structure) and thermostat, and from the solution of (18), one can find an electronic temperature  $T_e$ , which characterizes the Fermi distribution (see (5) and (8)).

Indeed, within the self-consistent consideration of the problem, the phonon spectrum of nanoclusters has to be discrete. However, in order to provide an estimate for the kinetic temperature, we decided that it is possible to use a ‘mixed’ model, in which Debye frequency depends monotonically on the size of a particle (quasi-classical approximation). In our opinion, in this approach, the quantum-size contribution to the phonon spectrum does not lead to significant changes of the results for clusters consisting of hundreds atoms. (Reasonable accuracy of the expression (21) was demonstrated in experiment [35] where X-ray scattering was studied on gold clusters with diameters ranging from 1.5 to 4.3 nm.)

When considering a transition from massive metal to small metal cluster, input parameters should depend on system’s sizes. The

formula (20) is rather sensitive to the choice of parameters (for example, to the sound velocity, whose determination can be considered as another problem). Therefore, in this paper, we only make an attempt to estimate electron kinetic temperature in small cluster through which the tunnel current flows.

#### 4. Results and discussion

We consider Au discs of monoatomic thickness whose radii vary in the range  $2R \simeq \{1, 8.5\}$  nm and which contain  $\simeq \{14, 10^3\}$  atoms. Similarly, the spherical clusters with  $2R \simeq \{1.4, 2.8\}$  nm contain  $\simeq \{100, 600\}$  atoms. (In Refs. [5,6] cluster sizes are given in terms of monolayer numbers; therefore, we used normalized curve from Fig. 1 of Ref. [42] in order to express these sizes in terms of nanometers.)

In this work calculations are performed for structures based on clusters, for which  $I-V$  curves were measured at different temperatures, namely, for a disc with a diameter  $2R = (4 \pm 0.5)$  nm and thickness  $H \approx 0.3$  nm [3] and for spheres with  $2R = (2 \pm 0.35)$  nm [5,6]. Because of the uncertainty of sizes and number of atoms, we used the Jellium model and found that disc and sphere contain 240 and 248 atoms, accordingly. Then  $\tilde{E}_C = 0.44$  and 1.31 eV for the disc and sphere, respectively. In spite of the fact that volumes of these two clusters are nearly the same, a difference between their shapes produces a significant mismatch in  $\tilde{E}_C$ .

The calculations of the characteristic Coulomb energy of charging  $\tilde{E}_C$ , using self-capacitance of a single granule in vacuum, demonstrated [7] that these  $C$  values are too small for the width of the current gap to be explained. Therefore we determine the characteristic energy of clusters charging as  $\tilde{E}_C = e^2/C_{\text{eff}}$ . Effective capacitance  $C_{\text{eff}} = (R + \delta)$  is used in order to explain experimental results for spherical clusters. The additional small quantity  $\delta$  is caused by an increase of radius of the charging electron ‘cloud’. For gold  $\delta$  is equal approximately to 0.1 nm [41]. The most obvious example is the case of a disc, since almost half of the disc surface contacts to the dielectric film with  $\epsilon = 3$ . In this case  $C_{\text{eff}}$  is estimated as a capacitance of the spheroid with minor axis of length  $H$ . A major axis  $a$  is obtained from a condition  $\pi R^2 H = 4\pi a(H/2)^2/3$ . Thus, we have

$$C_{\text{eff}} = \frac{1 + \epsilon}{2} \frac{\sqrt{a^2 - (H/2)^2}}{\arccos(H/2a)}.$$

We note that the value of the capacitance is sensitive to the shape of the granule surface so that even small deviation from the spherical shape can change significantly the capacitance.

Clusters under consideration are non-magic. The Fermi level  $\mu^g$  and levels of lowest unoccupied  $\epsilon^{\text{LU}}$  and occupied  $\epsilon^{\text{HO}}$  electron states in the clusters are in line. Spectrums were calculated and reported in our earlier works [7,8].

Taking into consideration the conditions of experiments [3–6] and the symmetry of measured  $I-V$  curves, the following numbers have been chosen as input parameters in our calculations:  $d_e = 1$  nm,  $d_c = 0.1$  nm (Fig. 1), and  $\beta \equiv I^e/I^c = 2$  and  $1/2$  for structures based on a disc and sphere, accordingly.

Calculated  $I-V$  curves for different magnitudes of a parameter  $\beta$  were analyzed in Ref. [7] where the effects of broadening and over-heating were neglected. As follows from the expression

$$\Delta V_g = \frac{\tilde{E}_C}{2e} \left( \frac{1}{2 - \eta^+} + \frac{1}{2 - \eta^-} \right),$$

the width of the current gap is independent on  $\beta$ . However, the current jumps are very sensitive to the value of  $\beta$  which, in its turn, has no influence on threshold voltages. With the growth of  $\beta$ , the slope of the parts of  $I-V$  curves which correspond to  $V > 0/V < 0$ , de-

creases/increases, respectively. For granular films a theory of Ref. [43] gives a similar result, however, measurements of Ref. [43] demonstrate the influence of tunneling resistances (in other words, of parameter  $\beta$ ) on the current gap width.

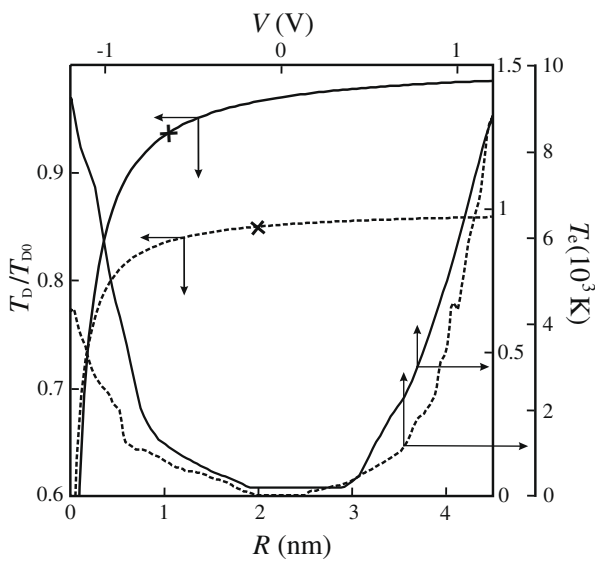
We perform calculations for gold clusters with the electron-phonon interaction constant  $U_{e-ph} = 1$  eV [25], the Debye temperature  $T_{D0} = 150$  K, the density of Au  $\rho = 19.3 \times 10^3$  kg/m<sup>3</sup>, and the 'average' sound speed  $s = 1500$  m/s [36].

The size dependences of the Debye temperature  $T_D(R)$  were analyzed taking into account Eq. (21). The actual forms  $T_D(R)$  in a wide range of sizes are plotted in Fig. 2. Different asymptotic behaviors of these two curves is due to the fact that in Eq. (21) at  $R \rightarrow \infty$ , one has  $S/\Omega \rightarrow 0$  for spheres and  $2/H$  for discs.

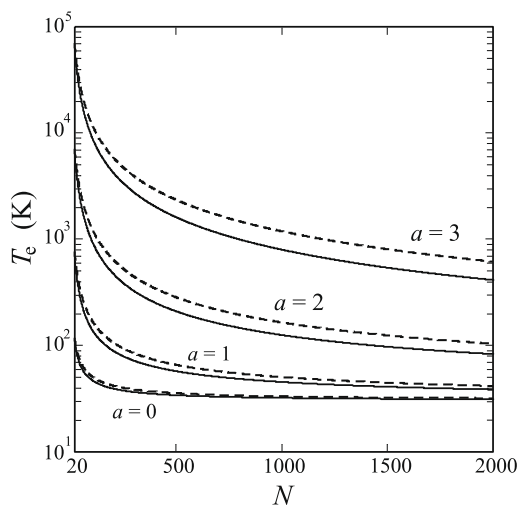
The injected power leads to the overheating of the electron subsystem. With the increase of the bias voltage  $V$  the number of elec-

trons relaxing in the granule increases significantly. Among them are all the electrons with energies in the interval  $e\eta V$  below the Fermi level of the granule, since the flow of tunneling electrons increases from low lying levels, thereby, involving large number of conductivity electrons to the relaxation process. The granule does not fragmentize during the significant overheating of the electron subsystem, because the  $I-V$  curves are reproduced during the cyclic changes of the bias voltage [3–6].

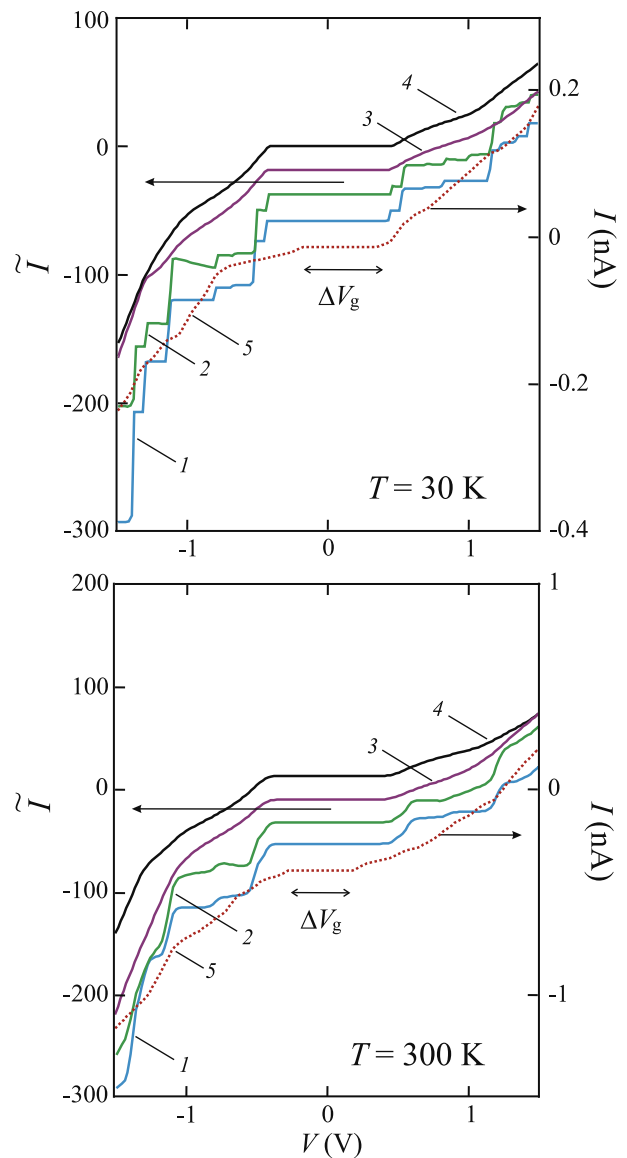
The dependences  $T_e(V)$  for two structures based on sphere and disc (temperature of ions 5 K and 30 K, accordingly) are also plotted in Fig. 2. One can observe strong dependence of electronic kinetic temperature on voltage. Heating of electrons in a disc is much more intensive than in a sphere: the corresponding temperature is almost one order of magnitude higher and it achieves thousands of Kelvin. It is of interest to note that the tunneling cur-



**Fig. 2.** Size dependences of the Debye temperature  $T_D(R)$  in spheres (solid line) and discs (dashed line). Values of  $T_D(R)$  are depicted ( $\times$ ) at the curves, and these values are then used in calculations of electron heating in the sphere and disc. For these two clusters, voltage dependences of electronic kinetic temperature  $T_e(V)$  are presented too.



**Fig. 3.** Size dependences of the electronic kinetic temperature  $T_e(N)$  in spheres (solid line) and discs (dashed line) for different values of injected power  $\mathcal{P} = 10^a \mathcal{P}_0$ ,  $\mathcal{P}_0 = 10^{-12}$  W.  $N$  is the number of atoms.

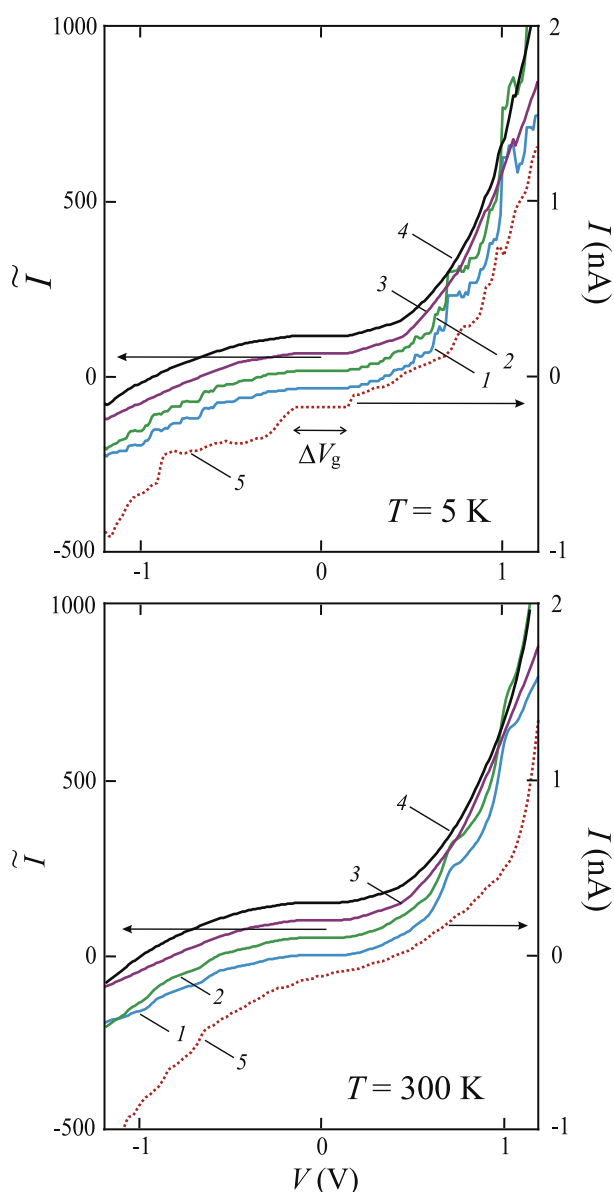


**Fig. 4.** Calculated  $\tilde{I}-V$  curves for structure based on spherical cluster of the radius of 1 nm at two values of two-temperature of structure and 1 -  $T_e = T_i = T$  (i.e. without the account of broadening and overheating), 2 - with the account of only overheating, 3 - with the account of only broadening, 4 - with the account of both the broadening and overheating. 5 - Experimental curves [5,6]. For presentation purposes, the curves are shifted slightly in a vertical direction. In the experiments, the width of the current gap  $\Delta V_g$  is  $0.55 \pm 0.1$  V at  $T = 30$  K [42] and 300 K [6].

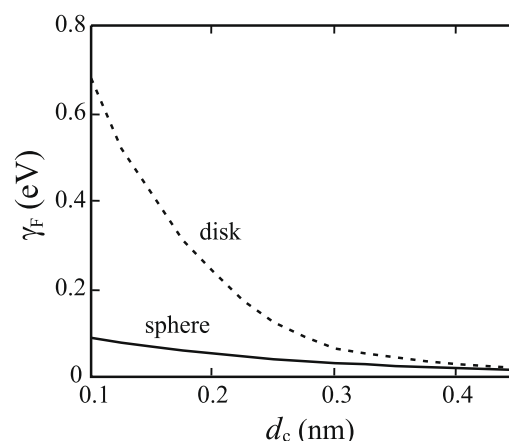
rent in 1 pA only is provided by  $\sim 10^6$  of electrons per second that is a significant number for the granule, which contains hundreds of conductivity electrons.

In the recent article [16] a thermo- and photoemission characteristics of Ag and Au granular films under the action of the pico- and femtosecond laser pulses were investigated. One of the conclusions of [16] is the fact of increase of the kinetic electron temperature with decrease of cluster size for  $\mathcal{P} = \text{const}$ . Also the estimation of electron temperature in 2800 K for Au granule with 5 nm diameter was given. The results of our calculations, which are presented at Figs. 2 and 3, are in agreement with these conclusions.

The calculated  $I$ – $V$  characteristics for structures, based on spherical and disc clusters, are plotted in Figs. 4 and 5. At low temperatures, the calculated values of gap width  $\Delta V_g$  are in accordance with the experimental data for a structure on disc-like cluster



**Fig. 5.** Calculated  $\tilde{I}$ – $V$  curves for structure based on cluster-disc of the radius 2 nm at two values of two temperature of structure and  $1 - T_e = T_i = T$  (i.e. without the account of broadening and overheating), 2 – with the account of only overheating, 3 – with the account of only broadening, 4 – with the account of both the broadening and overheating, 5 – Experimental curves [3]. In the experiments, the width of the current gap  $\Delta V_g = 0.3 \pm 0.075$  V at  $T = 5$  K and  $\Delta V_g \rightarrow 0$  at  $T = 300$  K.



**Fig. 6.** Calculated dependences of 'work subband' broadening  $\gamma_F$  vs. granule-collector distance for three-electrode structure based on the sphere with  $R = 1$  nm (solid line) and disc with  $R = 2$  nm (dashed line).

(Fig. 5). An approximately 1.5 times difference for a structure on a spherical cluster (Fig. 4) can be possibly attributed to the fact that we have neglected the mutual capacities effect (the dependence of  $\tilde{E}_c$  on the mutual location of the electrodes within the tunnel structure).

The broadening of the levels mimics a quasi-continuous spectrum in a cluster. The calculation of broadening  $\gamma(\varepsilon)$  is performed for disc in absence of a bias of a voltage. This approximation has to be considered as an estimate of a minimum broadening for the whole  $\tilde{I}(V)$  curve (here  $\beta = \Gamma^e/\Gamma^c$  is input parameter). In the disc-shaped dot, the electron states are realized only with 'subbands'  $n_z = 1$  and 2. States with  $n_z = 1$  almost do not decay. The broadening of the levels with  $n_z = 2$  equals approximately 0.7 eV. Fig. 6 demonstrates the dependence of broadening on the width of the tunnel junction. Estimation of broadening in spheres is rather rough, since it does not take into account obvious *three-dimensionality* of the tunnel junctions.

It can be noted that it is not possible to calculate separately the tunnel rates  $\Gamma^e$ ,  $\Gamma^c$  and values of broadening  $\gamma^e$ ,  $\gamma^c$  for the disc in the structure with two tunnel junctions. Only in the case of noninteracting electrons and one gate model, the tunneling probability from level  $\varepsilon_m$  to  $j$ th electrode is  $\Gamma_j(\varepsilon_m) = 2\pi\gamma_{mj}^2\rho_j(\varepsilon_F)/\hbar$ , where  $\rho_j$  is the density of final state [44]. Moreover, in order to calculate  $I$  we have to know  $P_0$  (see (3)), the problem of computation of  $P_0$  being rather hard.

Width  $\Delta V_g$  for non-magic clusters is determined only by charging energy  $\tilde{E}_c$ . An overheating in current gap is not substantial, because injected energy is minimal. At  $T = 300$  K our calculation gives  $\Delta V_g$ , in satisfactory agreement with experiment for structure based on the disc. The result for a disc however is quite sensitive to the temperature. It can be due to the change of cluster shape and its metallic properties because of the thermal fluctuations.

Steps of the Coulomb and quantum staircases are clearly visible outside the region of current gap in  $I$ – $V$  curves, which are calculated neglecting the broadening and the overheating. The broadening and the overheating give similar results in smoothing of staircases for granule-molecule at low temperatures (however, a role of the broadening is much more significant). It is checked out by plotting the differential conductance  $d\tilde{I}/dV$ . Unfortunately, in experiments [3–6], the differential conductance  $dI/dV$  was not reported.

## 5. Conclusion

In this work the semi-empiric estimations of two mechanisms are performed: (i) broadening of electronic levels due to a tunnel

effect, (ii) heating of electronic gas in the isolated metal clusters in presence of bias voltage. The calculations are carried out for two gold clusters of close volume and different shapes (cylindrical and spherical).

A calculation scheme of  $S$ -matrix poles for the broadening effect in simplest model of rectangular barriers of three-electrode structure is suggested. For monoatomic disc of Au, containing approximately 250 atoms ( $\Delta\epsilon_F \approx \{0.2, 0.5\}$  eV [8]), the broadening of 'work subband'  $\gamma_F \approx 0.7$  eV ( $\Delta\epsilon_F$  and  $\gamma_F$  are the difference between discrete levels and the 'average' broadening of the levels in the vicinity of the granule's Fermi level, accordingly). Due to the small thickness of right barrier ( $d_c = 0.1$  nm), calculations lead to a noticeable broadening (Fig. 6). We expect that  $\gamma_F$  is weakly dependent on bias voltage in the range  $\pm 1$  V, because the height of tunnel barriers  $W_0 = 5.13$  eV.

In the framework of two-temperature model of metal cluster, and by using a size dependence of the Debye frequency, the effective electron temperature vs. bias voltage is found approximately. For helium temperature of ion subsystem, the heating temperature of electrons in a quantum disc is almost one order of magnitude higher than that in a sphere; it achieves thousands of Kelvin. Note that results for electron temperature in the clusters, presented in Fig. 2, are somewhat overestimated, because we did not take into account the process of heat transfer from the metal cluster to the substrate. Nevertheless, our simple scheme of electron heating gives the size-dependent electron temperature that is in qualitative agreement with the experimental results for free clusters [33] and granular films [16].

We suggest an explanation for the effect of smoothing of current-voltage curves in structures based on clusters consisting of accountable number of atoms which was observed experimentally at low temperatures. We believe that smoothing effect can be attributed to the electron levels broadening. Effect of hot electrons is not almost noticeable at calculated  $\tilde{I}-V$  curves.

The indicated mechanisms can violate the basic inequalities, which have to be fulfilled for single-electronic devices to be able to work

$$\tilde{E}_C, \Delta\epsilon_F \gg k_B T,$$

because, in these conditions, it is necessary to replace  $\Delta\epsilon_F$  by  $\Delta\epsilon_F - \gamma_F$  and  $T$  by  $T_e$ .

Fabrication of elements stable in terms of their sizes and shapes is one of the key problems of nanoelectronics. For technological purposes, the use of structures based on metallic clusters is problematic from the viewpoint of reproducibility, because these clusters are self-organized both in sizes and shapes. Hopefully, this problem can be solved on a picelectronics level by using individual atoms of metal, each atom being covered by a dielectric shell (for instance  $\text{Zn}@C_{28}$  clusters [45]). This approach seems to be more perspective, since it is easier to control tunneling contacts between atoms. It turns out to be a difficult task to describe a device based on such a cluster by using simple models; in particular, because it is not possible to use a charging energy  $\tilde{E}_C$  as an informative parameter. For this purpose it is necessary to know an electron affinity and ionization potential of metal atom in the shell of carbon atoms. Moreover there will be no effect of overheating owing to the lack of a free electron gas in the  $\text{Zn}@C_{28}$ .

A thermoemission current depends exponentially on the ratio of granule electron work function and the kinetic temperature. Change of current is substantial, provided that the temperature is changed in tens of times. We suppose that the broadening of the

levels must be also taken into account for the proper description of thermo- and photoemission in similar structures [16].

## Acknowledgments

We are grateful to W.V. Pogosov for reading the manuscript. This work was supported by the Ministry of Education and Science of the Ukraine.

## References

- [1] E.S. Soldatov, V.V. Khanin, A.S. Trifonov, S.P. Gubin, V.V. Kolesov, D.E. Presnov, S.A. Yakovenko, G.V. Khomutov, A.N. Korotkov, *Uspekhi Fiz. Nauk* 168 (1998) 217 (*Physics-Uspekhi* 41 (1998) 202).
- [2] J. von Delft, D.C. Ralph, *Phys. Rep.* 345 (2001) 61.
- [3] B. Wang, X. Xiao, X. Huang, P. Sheng, J.G. Hou, *Appl. Phys. Lett.* 77 (2000) 1179.
- [4] J.G. Hou, B. Wang, J. Yang, X.R. Wang, H.Q. Wang, Q. Zhu, X. Xiao, *Phys. Rev. Lett.* 86 (2001) 5321.
- [5] T. Ohgi, D. Fujita, *Physica E* 18 (2003) 349.
- [6] T. Ohgi, D. Fujita, *Surf. Sci.* 532–535 (2003) 294.
- [7] V.V. Pogosov, E.V. Vasyutin, *Nanotechnology* 17 (2006) 3366.
- [8] V.V. Pogosov, E.V. Vasyutin, A.V. Babich, *Pisma v Zh. Tekhn. Fiz.* 33 (2007) 1 (*Tech. Phys. JETP* 4 (1957) 173).
- [9] C.W.J. Beenakker, *Phys. Rev. B* 44 (1991) 1646.
- [10] D.V. Averin, A.N. Korotkov, K.K. Likharev, *Phys. Rev. B* 44 (1991) 6199.
- [11] Y. Meir, N.S. Wingreen, *Phys. Rev. Lett.* 68 (1992) 2512.
- [12] V.L. Ginzburg, V.P. Shabanskii, *Dokl. Akad. Nauk SSSR* 100 (1955) 445.
- [13] M.I. Kaganov, I.M. Lifshitz, L.V. Tanatarov, *Zh. Eksp. Teor. Fiz.* 31 (1956) 232 (*Sov. Phys. JETP* 4 (1957) 173).
- [14] Z. Lin, L.V. Zhigilei, V. Celli, *Phys. Rev. B* 77 (2008) 075133.
- [15] Y.-F. Zhang, J.-F. Jia, T.-Z. Han, Z. Tang, Q.-T. Shen, Y. Guo, Z.Q. Qiu, Q.-K. Xue, *Phys. Rev. Lett.* 95 (2005) 096802.
- [16] A. Gloskovskii, D.A. Valdaitsev, M. Cinchetti, S.A. Nepijko, J. Lange, M. Aeschlimann, M. Bauer, M. Klimenkov, L.V. Viduta, P.M. Tomchuk, G. Schönhense, *Phys. Rev. B* 77 (2008) 195427.
- [17] G. Kopidakis, C.M. Soukoulis, E.N. Economou, *Phys. Rev. B* 49 (1994) 7036.
- [18] S.-X. Qu, A.N. Cleland, M.R. Geller, *Phys. Rev. B* 72 (2005) 224301.
- [19] L. de la Vega, A. Martén-Rodero, N. Agrait, A. Levy Yeyati, *Phys. Rev. B* 73 (2006) 075428.
- [20] R. D'Agosta, Na Sai, M. Di Ventra, *Nano Lett.* 6 (2006) 2935.
- [21] M. Galperin, M.A. Ratner, A. Nitzan, *J. Phys.: Condens. Matter* 19 (2007) 103201.
- [22] E.D. Belotski, S.P. Luk'yanets, P.M. Tomchuk, *Zh. Eksp. Teor. Fiz.* 101 (1992) 163 (*Sov. Phys. JETP* 74 (1992) 88).
- [23] R.D. Fedorovich, A.G. Naumovets, P.M. Tomchuk, *Phys. Rep.* 328 (2000) 73.
- [24] Y. Bilotsky, P.M. Tomchuk, *Surf. Sci.* 602 (2008) 383.
- [25] N. Singh, arXiv:cond-mat/0702331.
- [26] M. Ovadia, B. Sacepe, D. Shahar, *Phys. Rev. Lett.* 102 (2009) 176802.
- [27] V.V. Kresin, Yu.N. Ovchinnikov, *Phys. Rev. B* 73 (2006) 115412.
- [28] R. Pushpa, U. Waghmare, S. Narasimhan, *Phys. Rev. B* 77 (2008) 045427.
- [29] B. Rethfeld, A. Kaiser, M. Vicanek, G. Simon, *Phys. Rev. B* 65 (2002) 214303.
- [30] B. Rethfeld, K. Sokolowski-Tinten, D. von der Linde, S.I. Anisimov, *Appl. Phys. A* 79 (2004) 767.
- [31] L. Jiang, H.-L. Tsai, *J. Heat Transfer* 127 (2005) 1167.
- [32] G. Gantefor, W. Eberhardt, H. Weidele, D. Kreisler, E. Recknagel, *Phys. Rev. Lett.* 77 (1996) 4524.
- [33] M. Maier, M. Schatzke, G. Wrigge, M.A. Hoffmann, P. Didier, B.V. Issendorff, *Int. J. Mass Spectrom.* 252 (2006) 157.
- [34] P.R. Couchman, F.E. Karasz, *Phys. Lett. A* 62 (1977) 59.
- [35] A. Balerna, S. Mobilio, *Phys. Rev. B* 34 (1986) 2293.
- [36] M.X. Gu, C.Q. Sun, Z. Chen, T.C. Au Yeung, S. Li, C.M. Tan, V. Nosik, *Phys. Rev. B* 75 (2007) 125403.
- [37] C.-H. Zhang, F. Kassubeck, C.A. Stafford, *Phys. Rev. B* 68 (2003) 165414.
- [38] D.F. Urban, C.A. Stafford, H. Grabert, *Phys. Rev. B* 75 (2007) 205428.
- [39] A. Maradudin, R. Wallis, *Phys. Rev.* 148 (1966) 945.
- [40] A.I. Baz', Ya.B. Zel'dovich, A.M. Perelomov, *Scattering, Reactions and Decays in Nonrelativistic Quantum Mechanics*, Nauka, Moscow, 1971 (in Russian).
- [41] V.V. Pogosov, V.P. Kurbatsky, E.V. Vasyutin, *Phys. Rev. B* 71 (2005) 195410.
- [42] T. Ohgi, H.-Y. Sheng, Z.-C. Dong, H. Nejo, D. Fujita, *Appl. Phys. Lett.* 79 (2001) 2453.
- [43] H. Imamura, J. Chiba, S. Mitani, K. Takanashi, S. Takahashi, S. Maekawa, H. Fujimori, *Phys. Rev. B* 61 (2000) 46.
- [44] E.O. Kane, in: E. Burstein, S. Lundqvist (Eds.), *Tunneling Phenomena in Solids*, Plenum, New York, 1969.
- [45] M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, *J. Am. Chem. Soc.* 107 (1985) 3902.