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A NUMERICAL ANALYSIS OF PROCESSES IN ORGANIC ELECTROLUMINESCENT STRUCTURE WITH METAL NANOPARTICLES

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A simple model for thin film organic electroluminescence in single layered one-dimensional cell with metal nanoparticles is developed, assuming direct excitation of luminophor molecules by electron impact. The values and behaviour of calculated curves for brightness and efficiencies correlate with experimental data. The insertion of metal nanoparticles into active volume of electroluminescent cell leads to the increase of the average electric field inside the cell and to the decrease of the threshold of electroluminescence and stimulated radiation due to improved conditions of electron tunneling as a result of potential barriers shape change.

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1. Introduction

Organic solid thin film structures are very promising for the application in manifold optoelectronic devices [1]. One of the main requirements to them is a high homogeneity of organic films. However, a lot of nonuniform structures [1-8] with a high energy transformation performance was offered. One of the methods of the nonuniform structure creation is introducing of metal or semiconductor nanoparticles into an organic luminophor [8,9]. The presence of metal nanoparticles makes the dielectric organic material conductive [9]. In such systems a non-cavity lasing [10] was obtained. We have developed an electroluminescent structure on the basis of MEH-PPV with silver nanoparticles with good light performances. But, mechanism of electroluminescence threshold decreasing and efficiency increasing is still unknown.

We offered earlier [11,12] a physical model describing the processes of electric energy transformation by organic luminophor molecules. This model is based on approach that organic luminophor molecules excitation is given by inelastic interactions with electrons, emitted from the cathode as a result of tunneling, and accelerated by an electric field. The obtained dependences, for example, of the luminescent emission distribution in a depth of the electroluminescent cell, as well as the electroluminescence energy efficiency dependence on the electric field have shown good correspondence to the experimental data [13,14] that is a good confirmation of our approach adequacy. The calculations have allowed to conclude [15] that it is possible to receive the stimulated radiation in thin electroluminescent cell on the basis of organic compounds at electrical excitation under substantially accessible values of electric field intensity using a low value of injection barrier. The purpose of the present work is the analysis of processes in the electroluminescent cell with metal nanoparticles. First of all, we are interested in their influence on the emissive properties, the electric current, and on the possibility to obtain the stimulated radiation.

2. Physical model

We consider the structure representing a layer of organic light-emitting substance with metal nanosized blobes, by thickness d, placed in electric field E between metal electrodes with potential

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difference *U*. All blobs are distributed over the cell evenly, i.e. placed on distance d_1 from each other in directions along the electric field (*x*) and perpendicularly to it, and have identical diameter d_2. We assume, that luminophor molecules with concentration *N* are embedded into a certain dielectric medium, and an efficient energy transfer from the medium playing a role of the energy accumulator, on the impurity (luminophor) takes place in the system. The typical examples are doped organic crystals and conjugated polymer compounds with embedded organic molecules. The supposed permittivity $\varepsilon = 3.0$ is a typical value for organic mediums. The presence of a dielectric at the space between electrodes reduces an electric field. In the presence of dielectric the injection barrier is depressed on quantity of an electron affinity of the dielectric, and increases little owing to the reduction of image forces overlapping. We suppose potential injection barrier height Ψ taking into account the dielectric influence.

The introduction of nanoparticles into the electroluminescent cell will result in redistribution of an electric field inside the cell. The cathode and nanoparticle electron potential barriers will have a finite width in this case, and at the defined d_1 values the probability of electron tunneling through such barrier will be distinct from 0 (for simplification and owing to preferred tunneling of electrons which kinetic energy along the electric field is close to a Fermi level, we assume that the potential barriers are one-dimensional). Note, that in the considered two-dimensional conductive ensemble Coulomb blockade will not play such a role as it takes place in single island chains [16]. In such a multilevel structure two mechanisms of electron transfer are possible [17] such as the coherent electronic transport if the tunneling factors are high enough, and two steps transport if the resistance of tunneling barriers is high. As we were interested in the case of strong fields, we did not take into account charge effects.

We assume, that electrons leave the cathode which surface coincides with the plane $x = x_0 = 0$, and then they are accelerated by applied electric field *E*, passing a chain of the potential barriers between metal nanoparticles. At such a considered symmetry the excitation rate of luminophor molecules will be defined only by one spatial coordinate *x*.

In the common view the luminophor molecule excitation rate in point *X* will be defined by the following expression:

$$W(X) = \int_0^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \sigma(p_x, p_y, p_z)\frac{j(x, p_x, p_y, p_z)}{e}dp_x dp_y dp_z, \qquad (1)$$

where $\sigma(p_x, p_y, p_z)$ is the molecule excitation cross-section as a result of inelastic collision with electron having impulse projection values p_x,p_y,p_z, $j(x, p_x, p_y, p_z)$ is the current density in point *X*, *e* is the charge of electron.

The electron current density on metal/dielectric border is defined by the expression:

$$j(p_{x_0}, p_y, p_z) = f(p_{x_0}, p_y, p_z)D(p_{x_0}, E)v_{x_0}e, \qquad (2)$$

where $f(p_{x_0}, p_y, p_z)$ is the distribution function of electrons in cathode metal, $D(p_{x_0}, E)$ is the barrier permittivity coefficient for electrons with impulse p_{x0}, $v_{x0} = p_{x_0}/m$ is the electron velocity projection on *x* axis in a point $x=x_0$. It is supposed in the formula (2) that tunneling is carried out on vacant levels of the next nanoparticle, i.e. nanoparticle Fermi levels lay below the cathode Fermi level and are lowered in the applied field direction (distribution function for a nanoparticle free area $f^0=0$). Inverse tunneling at the presence of the applied electric field is supposed to be absent.

It is known, that the metal nanoparticles presence deforms the potential barrier shapes. In the case of small metallic particle size and distances between them the essential superposition of image forces takes place, and, generally, the shape of barrier will have rather complicated form depending on the sizes, shapes and relative location of the nanoparticles [19]. It is often accepted [18], that barrier has a parabolic form and potential barrier between nanoparticles in the absence of electric field is defined by the expression:

$$U_0(x) = \frac{gx_0^2}{2} - \frac{g(x - x_0)^2}{2}, \qquad (3)$$

where $2x_0 = d_1$ is the barrier width. In electric field E barrier becomes lower, its maximum is shifted:

$$U_E(x) = \frac{gx_0^2}{2} - \frac{g(x-x_0)^2}{2} - eEx\,. \tag{4}$$

However, such a potential barrier approximation can be applied only with some stipulations. The growth of such barrier width at the stationary value of its height results in the parabola increasing velocity reduction, and at high enough electric fields it will give to that calculated transparence values D and consequently, conductance current, will be higher for wider barriers, than for narrow (see Fig. 1, *a*), that is unreal. Thus, such a potential barrier representation is legal at low electric field values only though the high values are more interesting for us, especially regarding to reach the inverse density population of luminophor molecule levels. Therefore, we present the potential barriers between nanoparticles both as a parabola and a rectangle with d_1 width (see Fig. 1, *b*), that represents other extreme case which is not taking into account the potential barriers shape changes.

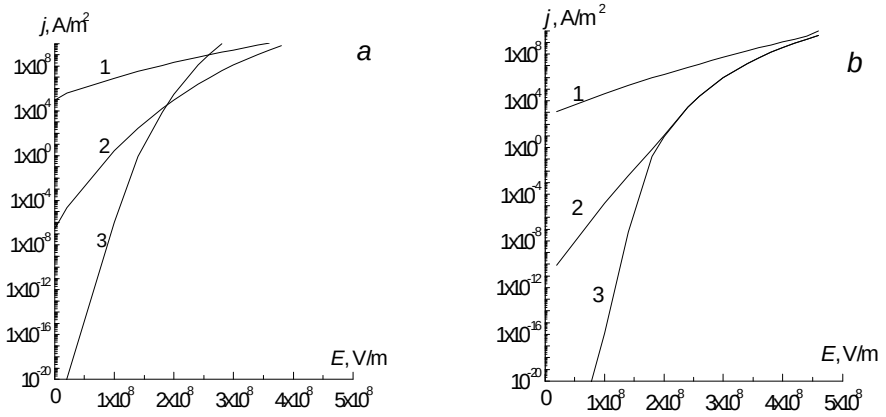

Fig. 1. Dependence of density of current j passing through the parabolic (a) and rectangular (b) barrier on applied electric field; Ψ=1 eV.

It is necessary to take into consideration also the electron emission from nanoparticles owing to tunneling electrons from them at high fields, and electron thermo-emission as a result of current warming up. The electronic gas temperature in metal nanoparticles may achieve 0.4-0.7 eV (i.e. about several thousands K), thus the film temperature may be close to environment temperature [18]. Nevertheless, it is known from experiments [18], that the thermo-emission current value is some orders lower, than the conductance current. So, the thermionic emission current will not influence essentially the excitation of molecules. Besides, only thermal electrons are the result of thermo-emission from metal while the electrons with energy of about 10 eV are most effective for excitation of organic compounds [20], so for reaching such energy thermo-electrons have to pass the comparable accelerating potential difference. It will require higher applied voltages at which electron tunneling is more essential.

The work function of nanoparticles is essentially higher, than for the special cathode, and current has exponential dependence on the work function, so it is possible to expect, that the tunneling current from nanoparticles will not essentially deposit to luminophor molecules excitation. According to our calculations this current differs at least three orders in the case of barrier height value Ψ = 2 eV and 1 eV for nanoparticles and cathode, correspondingly. Thus, the electron emission from nanoparticles also does not essentially affect the luminophor molecule excitation.

The calculation of $W(X)$ was carried out by a numerical integration of expression (3), using a function of degenerate Fermi gas as $f(p_{x_0}, p_y, p_z)$. The efficiency η was determined as a ratio of the total kinetic energy of the electrons leaving metal, and the energy of electron acceleration in luminophor by electric field. ββ-Dinaphtilethelene with typical for organic compounds spectral and kinetic characteristics [15] was used as luminophor. The electroluminescent cell with a thickness of 100 nm, dimensions of 1×2 mm, with aluminium cathode (E_f=*11,8* eV) was considered. The luminescence quenching by metal particles [21] was not taken into account.

3. Results and discussion

According to calculations, the increase of applied voltage between nanoparticles results in disappearance of the dependence of potential barrier width (i.e. values d_1), curves for conductance currents on Fig. 1, *b* are converged at values $E \sim 4.5 \times 10^8$ V/m. The difference between these two extreme cases of model barriers is essential at small fields while with the increase of E it becomes less considerable.

Fig. 2 (*a-d*) shows the calculated dependences of the cell volume averaged excitation rate W of luminophor molecules and fluence F of radiation from this cell in a direction perpendicularly to the applied field, which are compared to the similar data for the cell without nanoparticles [15]. It can be seen that stimulated radiation appears at significantly smaller applied voltage, than in electroluminescent cell without nanoparticles (curves *4* on Fig. 2). The most clearly it can be seen at efficiency curve (*e, f*). Note, that the zigzag behaviour of some calculated dependences in the region of low fields is connected with disproportional change of electrical power consumption and excitation rate of molecules. On the contrary (see Fig. 2, *f*), the threshold voltage U_{th} not so strongly depends on distance between nanoparticles (at the same values of averaged field). If we represent these dependences on electric field (Fig. 3, rectangular barrier), they become the same beginning from some field value. The reason of such a behaviour is apparently the increase of field in the cell with nanoparticles. The threshold of appearance of stimulated emission is lower due to nonrectangular barrier shape (Fig. 2).

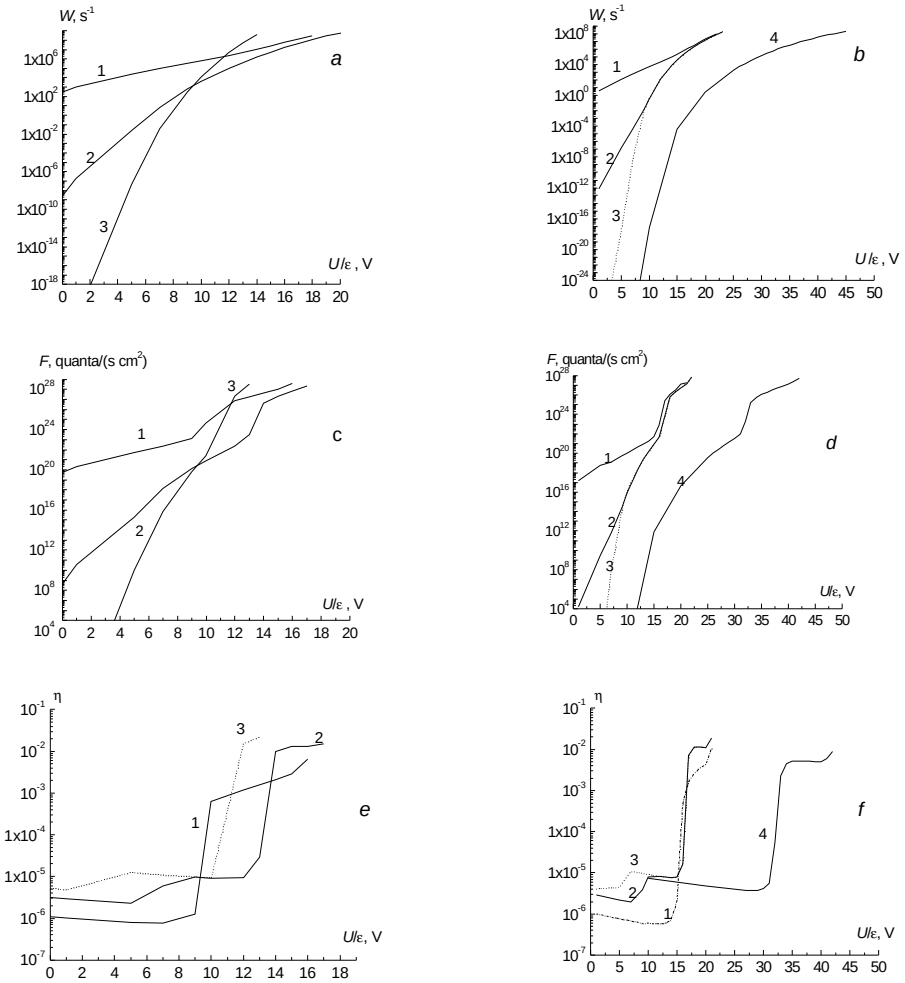

Fig. 2. Dependence of averaged excitation rate W (a, b), fluence F (c, d), and efficiency η (e, f) on applied voltage for electroluminescent cell with Ψ=1 eV, d=100 nm, d_2=d_1=2 (1), 5 (2),10 (3) and 0 nm (4) for parabolic (a, c, e) and rectangular (b, d, f) barrier.

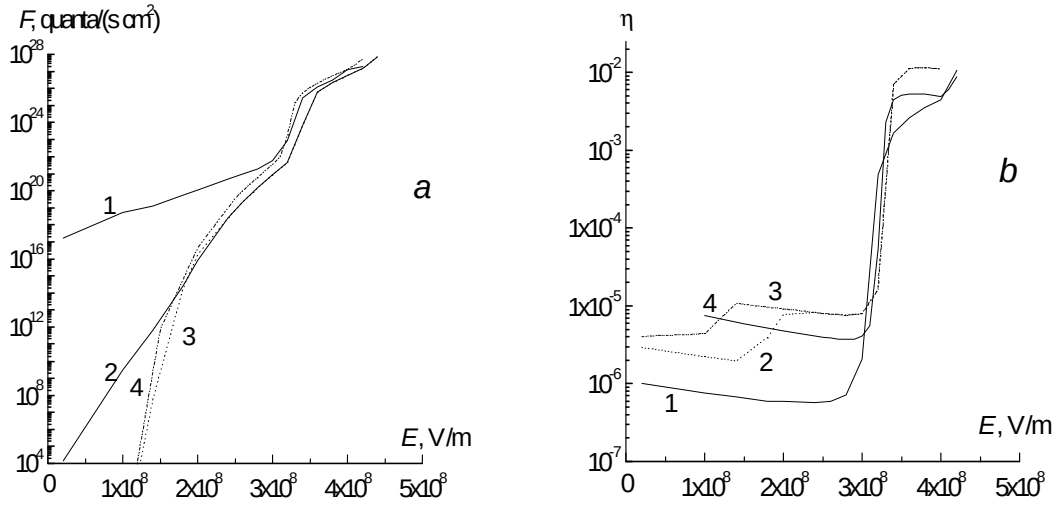

Fig. 3. Dependence of fluency F (a) and efficiency η (b) on applied electric field for the cell with Ψ=1 eV, d=100 nm, $d_2=d_1$=2 (1), 5 (2),10 (3) and 0 nm (4) for rectangular barrier.

The distribution of excitation on the cell depth shows the strong inhomogeneity at low applied voltages and at small values of distance between nanoparticles (Fig. 4). It is apparently due to the electron passage the several potential barriers with a finite width. Note that calculated dependences more adequately correspond to the transient excitation, in a stationary case at small fields the calculated dependences should have stepped character owing to Coulomb blockade.

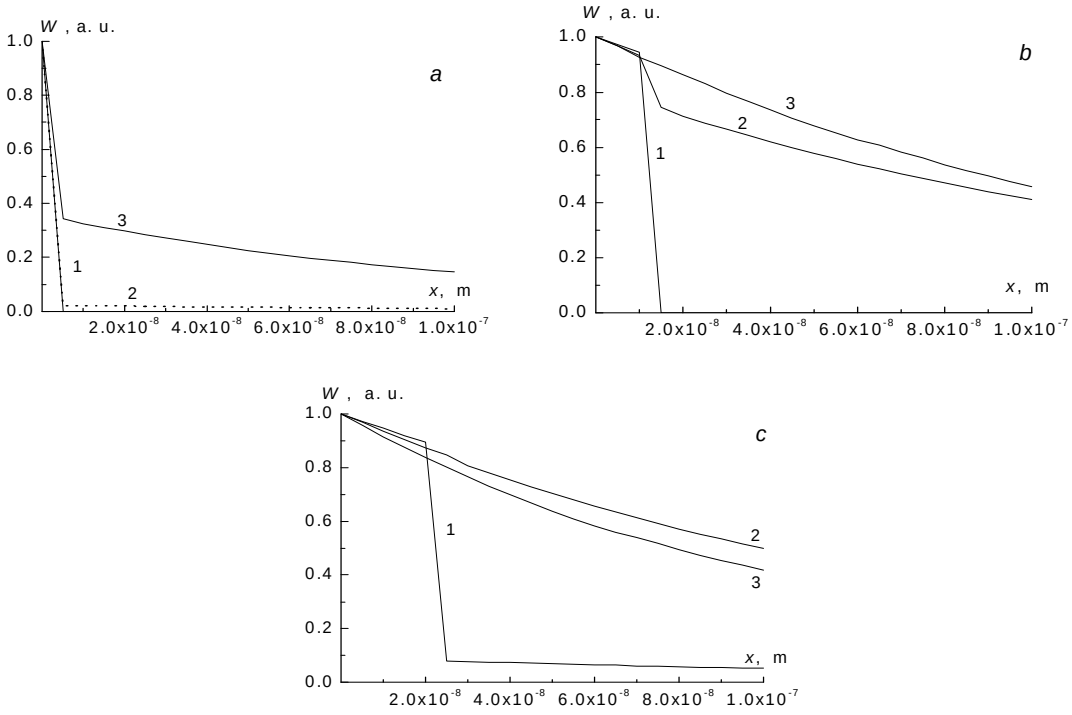

Fig. 4. Normalized distribution of excitation rate on the cell depth: a – $d_1=d_2$=2 nm, U/ε=10 (1), 15 (2), 20 (3) V; b – $d_1=d_2$=5 nm, U/ε =5 (1), 10 (2), 15 (3) V; c – $d_1=d_2$=10 nm, U/ε =5 (1), 10 (2), 20 (3) V.

The change of nanoparticles dimensions at the same distance between them apparently will result in the change of average field in electroluminescent cell (Fig. 5, *a*), and as a consequence, it will influence the dependences of radiation characteristics on applied voltage. However the size of nanoparticles affects these dependences also at the same fields (compare curves 1 and 5 in Fig. 5). The smaller nanoparticles concentration (greater nanoparticles diameter) results in the decrease of tunneling current due to growth of potential barrier and the field drop in many points on the cathode surface. This effect is more noticeable at low fields. Change of concentration of nanoparticles with the same diameter influences on electroluminescence characteristics at before-threshold fields (fig.5,e); at high fields these curves become closer.

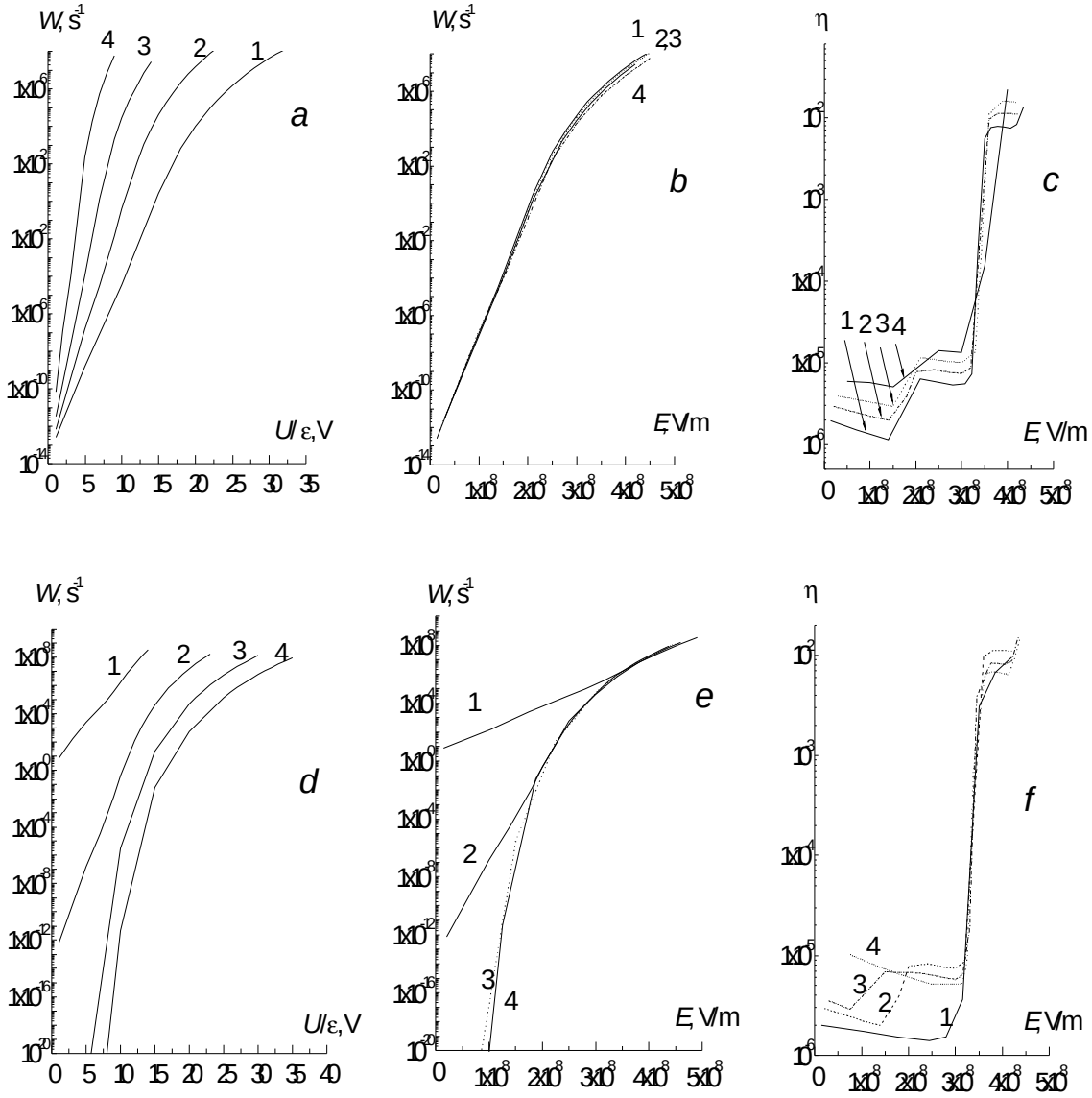

Fig. 5. Dependence of averaged excitation rate W (a,b,d,e) and stimulated radiation efficiency η (c, f) on applied voltage (a,d) and electric field (b,c,e,f) for cell with d_1=5 nm, d_2=2 (1), 5 (2), 10 (3) и 20 (4) nm (a-c), и d_2=5 nm, d_1=2 (1), 5 (2), 10 (3) и 20 (4) nm (d-f).

Fig. 6 illustrates the dependences of the maximal possible values of energy (η_{en}) and quantum (η_q) luminophore molecule excitation yield averaged over the cell volume. Both energy and

quantum yield are sensitive to value of Fermi level at rather low electric fields. Besides there is an optimal for reaching peak efficiency range of applied voltage, and their numerical values decrease with electric field. It is connected with acceleration of electrons up to the energies exceeding optimum, corresponding to maximal value of excitation cross section (10 eV [20]). The shift of maximums in the case of increase of concentration of nanoparticles with the same diameter can be explained by higher electric fields corresponding to optimal values of applied voltage, and some decrease of maximum heights is apparently connected with a change of active cell volume.

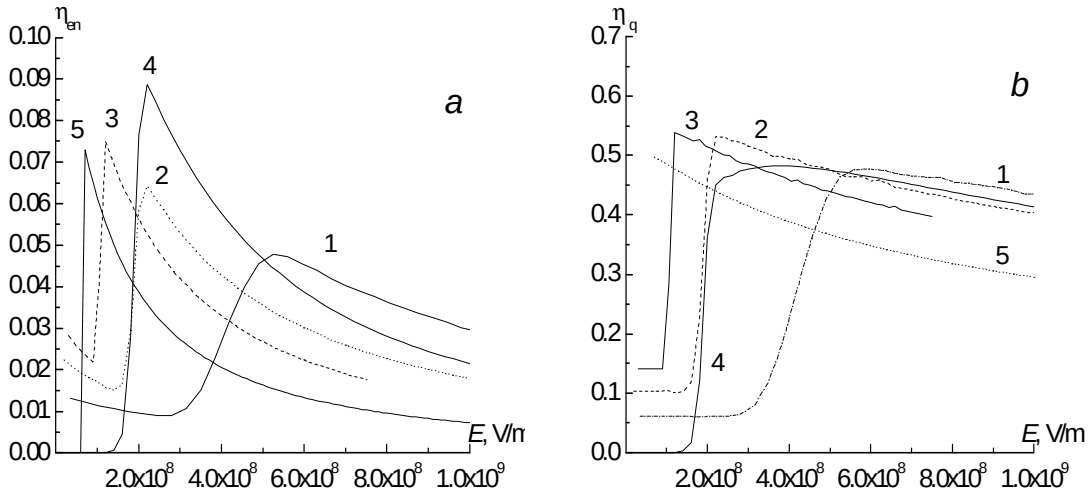

Fig. 6. Dependence of energy (a) and quantum (b) yield on applied electric field: Ψ=1 eV, d_1=5 nm (1-4), E_f=11.8 (1-3,5), 3 eV (4), d_2=2 (1), 5 (2,4), 10 (3), 0 nm (5).

2. Conclusion

The insertion of metal nanoparticles into active volume of electroluminescent cell leads to the increase of the average electric field inside the cell and to the decrease of the threshold of electroluminescence and stimulated radiation due to improving conditions of electron tunneling as a result of the change of potential barriers shape.

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