SIZE EFFECT IN THE LUMINESCENCE OF CRYSTALLOPHOSPHORUS

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Abstract

Size effects are inherent in all nanostructures and continue to attract the attention of not only physicists, but also biologists, physicians, and other specialties. In addition to fundamental problems, optical phenomena (including luminescence) in nanostructures are of great practical interest.

In the present work, an empirical multilevel model of the surface layer of solids is proposed, which explains all the observed size effects in nanostructures, including luminescence.

To obtain the equations, we used the method of nonequilibrium statistical thermodynamics.

The surface layer of a solid body consists of three layers - a de Broglie layer $d_0 \sim ((0.01\text{-}0.1)$ nm for metals) and layers $d(I)$ and $d(II)$. Size effects in a layer $d(I)$ are determined by the entire collective of atoms in the system (collective processes). Such "semiclassical" size effects are observed only in nanoparticles and nanostructures. The layer $d(II)$ should have many dimensional effects associated with a certain critical characteristic parameter: the mean free path of carriers in transport phenomena, the dimensions of domains/domain walls, the diameter of the Frank-Read loop for gliding dislocations, etc. When $h=d$ in the surface layer, a phase transition occurs. It is shown that the thickness of the surface layer $d(I)$ is determined by one fundamental parameter - the molecular (atomic) volume of a solid, which is different for metals, amorphous solids, glasses, and polymers. The proposed multilevel model of nanostructured states in solids, which explains all the observed size effects in nanostructures, including luminescence.

Keywords: nanostructure, multilevel model, size effects, luminescence, small particle, surface.

Introduction

Alexander Leonidovich Chizhevsky is one of the greatest scientists of the past century. It is quite logical, for those times, and what happened to Chizhevsky later. In 1942, he was arrested and sent to the Ivdellag concentration camp in the Sverdlovsk region, then stayed in the Karlag and Steplag camps in Kazakhstan. The repressions did not end there, because after the expiration of the camp period in 1950, he lived in a settlement in Karaganda for four years, and when the settlement expired, he still remained in Karaganda, permission to live in Moscow was never received. He had a job there at the Oncological Dispensary, where there was a decent laboratory, and he had the opportunity to conduct scientific research. In the same place, in Karaganda, he collaborated with the scientific research institute of the coal industry. The year 1958 has come. Chizhevsky was finally rehabilitated and he returned to Moscow. The famous "Chizhevsky Chandelier" is still popular with us, which ionizes the environment and can clean the air from dust. Ionization is often accompanied by luminescence, which we will discuss in this work.

Luminescence of small particles of crystal phosphors. The significant dependence of the luminescence efficiency of phosphors and the luminous efficiency of fluorescent lamps on the size of the phosphor grains has been paid attention for a very long time. In many works

(see reviews [1, 2]), the effects of a decrease in the luminescence brightness during grinding of crystal phosphors are explained by a sharp increase in the specific surface area of the phosphor in the layer and, accordingly, an increase in the scattering of exciting light, which ultimately leads to losses. Investigating the effect of grinding of halophosphate phosphors on the efficiency of fluorescent lamps, the authors of [3] found that it leads to a significant (up to 10-15%) decrease in the luminous efficiency of lamps. In [4], on the basis of the theory of "turbid" media, it was concluded that the reason for the decrease in the luminous efficiency of fluorescent lamps is the presence of "ultra-small" particles with sizes up to 3 microns, which increase the scattering of ultraviolet radiation back into the discharge gap of the lamps. However, this model does not agree with the results of studies on X-ray luminescence (see review [5]), where the critical grain size of the phosphor is 20–40 μm, from which the quantum yield of X-ray luminescence also drops sharply. Naturally, for particles of this size, X-ray scattering is negligible. Summarizing the results of the experimental data, the authors of [5] proposed an empirical dependence of the relative intensity I on the size r of the phosphor grains:

$$I = (1 - d/r)^3 \qquad (1)$$

where d is the thickness of the "dead" layer. According to the authors of [5], a "dead" layer is a layer from which thermalized (hot) charge carriers emerge to

the surface. The release of charge carriers from a depth d competes with their recombination at the emission centers, which leads to the quenching of luminescence in the "dead" layer (Fig. 1). The dimensional relationship between temperature and concentration quenching of intracenter luminescence was noticed long ago and was explained by us only in [6] on the basis of the thermodynamic approach (where Q ~ I and N ~ r) (Fig. 2). Within the framework of this approach, the following expression is obtained:
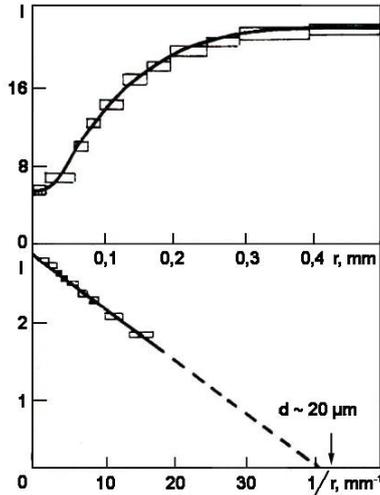
$$I = const = \exp(-2\sigma\upsilon/rRT) \approx const(1 - d_1/r), \quad (2)$$

where the depth of the "dead" layer is:

$$d_1 = 2\sigma\upsilon/RT . \quad (3)$$

Here σ is the surface tension of the phosphor grain, υ is its molar volume, R is the gas constant, T is the temperature. Since $(1-d/r)^3 \approx (1-3d/r)$, then equations (1) and (2) coincide up to a constant factor, and $d_1 = d/3$.

Figure 1 - Dimensional dependence of the intensity of X-ray luminescence on the grain size of the phosphor [5]
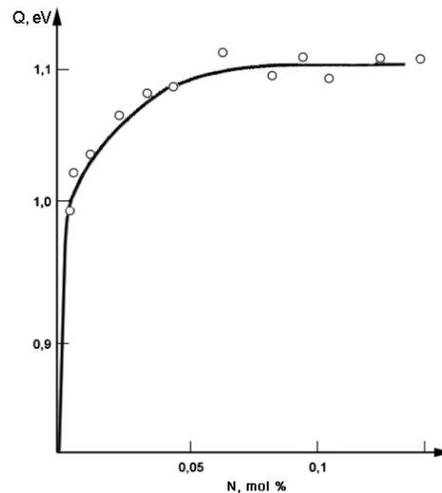

Figure 2 - Dimensional dependence of the activation energy Q on the concentration of luminescence centers for KBr-Tl [6]

Size effects in luminescence of crystal phosphors. The end of the 19th century coincided with the beginning of the development of nanotechnology, a distinguished feature of which was the size effects when the particle size decreased below certain critical sizes. The first review of size effects in luminescence, in our opinion, was made in [7]. An analysis was carried out on the size effects during the grinding of crystals of photo-X-ray-cathode-electroluminophores. Figures 3 and 4 show examples of these effects.

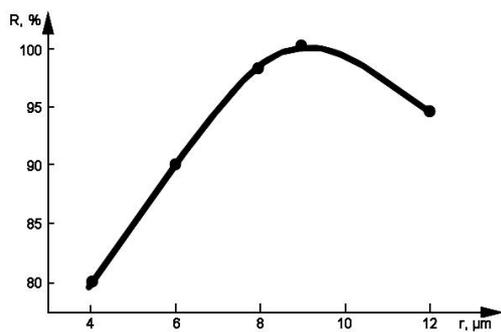It was stated that near the surface of an individual powder particle there is a layer with an increased content of biographical defects, the optical properties of which generally differ from the properties of an ideal surface. An increase in the number of these defects during powder grinding and a decrease in the average particle size leads to a decrease in the luminescence intensity and an increase in the absorption index of the material. However, the very mechanism of the size effect in the luminescence of various crystals remained unclear.
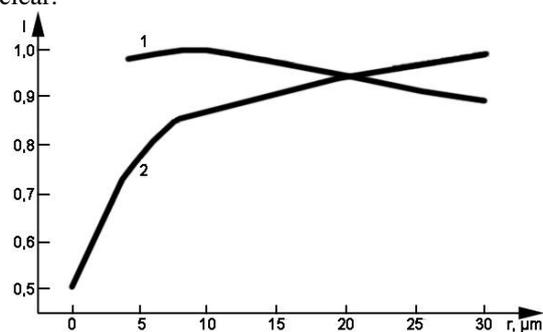

Figure 3 - Dependence of the brightness of cathodoluminescence (Zn, Cd)S - phosphor on the particle size [7]

Figure 4 - Dependence of the luminescence brightness of the X-ray phosphor ZnS on the particle size [7]

Size effect in the optical properties of semiconductor quantum dots

Semiconductor quantum dots (QDs) are usually called elementary (quasi-zero-dimensional) crystal structures bounded in all three directions, the sizes of which are comparable to the de Broglie wavelength for an electron (ae) and a hole (ah) or (u) with their Bohr radii of the Wa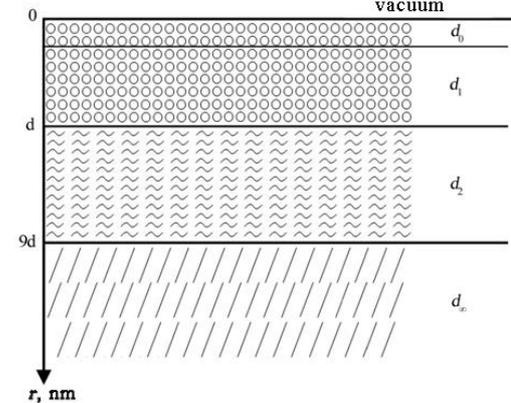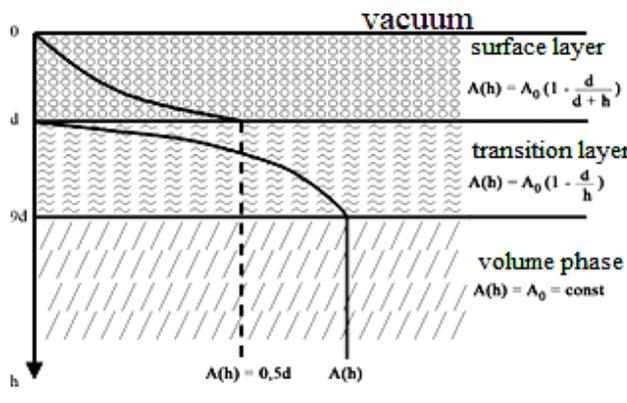nnier exciton Mott in this material [8-10]. The first experimental observations of the effect of dimensional quantization in the optical properties of semiconductor nanocrystals several nanometers in size were published in the early 1980s by Russian physicists (see literature reviews in [8-10]). As an example, Fig. 5 and 6 show the size effects in QDs of CdS and Ag2S crystals.
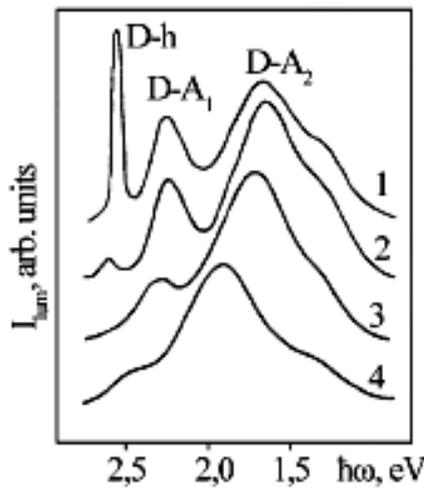
(1) R = 2.8 nm; (2) R = 7.4 nm; (3)
R = 3.3 nm; (4) R = 1.5 nm [10]

*Figure 5 - Stationary luminescence spectra
of CdS nanoparticles of different sizes.*

*Figure 6 - Dependence of the quantum size effect
in quantum dots Ag₂S [10]*

An analysis of the scientific literature [8-10] indicates a great interest in the study of size dependences and photophysical processes with the participation of localized states in semiconductor colloidal quantum dots CdS and Ag$_2$S. Interest in these structures is due to the possibility of their use in optoelectronic devices and biomedical applications. At the same time, the successful development of most applications using colloidal QDs is hindered by the lack of unambiguous data on detailed studies of the size dependence in the absorption and luminescence properties of Ag$_2$S QDs and the role of localized states in the formation of these properties.

An empirical model of the surface of solids

In [11-13], the proposed model of the surface layer of atomically smooth crystals is generalized. This model is shown schematically in Figure 7.


d_0 - de Broglie layer; d_1 - surface layer; d_2 -
transition layer; d_∞ - bulk phase layer

Figure 7 - Schematic representation of the surface layer

The de Broglie layer $d_0 = \lambda_{dB} = \hbar/p$ for metals ranges from 0.01 nm to 0.1 nm. Quantum dimensional effects begin in this layer. The main quantum-dimensional structures include structures with a two-dimensional electron gas - epitaxial films, MIS structures, heterostructures, etc .; structures with one-dimensional gas - quantum threads or wires; structures with a zero-dimensional gas - quantum dots, boxes, crystallites [14]. To determine the thickness of the surface layer of various compounds, we used the dimensional dependence of the physical property A(r) Layer d(I) = d is described by the dependence:

$$A(r) = A_0 - \left(1 - d/(d+r)\right), \quad d_0 \leq r \leq d. \quad (4)$$

In the d(I) layer with pure metal atoms, there is a reconstruction and relaxation associated with the rearrangement of the surface [15]. For gold, the lattice constant is d (I) = 0.41 nm and the surface is rearranged at a distance $(d(I)_{Au} = 1.2/0.41 \approx 3)$ of three atomic monolayers. The size effects in the d(I) layer are determined by the entire group of atoms in the system (collective processes). Such "semiclassical" size effects are observed only in nanoparticles and nanostructures [16]. Layer d(II) is described by the dependence:

$$A(r) = A_0 - \left(1 - d/r\right), \quad r \gg d. \quad (5)$$

The parameter d is related to the surface tension σ by the formula:

$$d = 2\sigma\upsilon/RT. \quad (6)$$
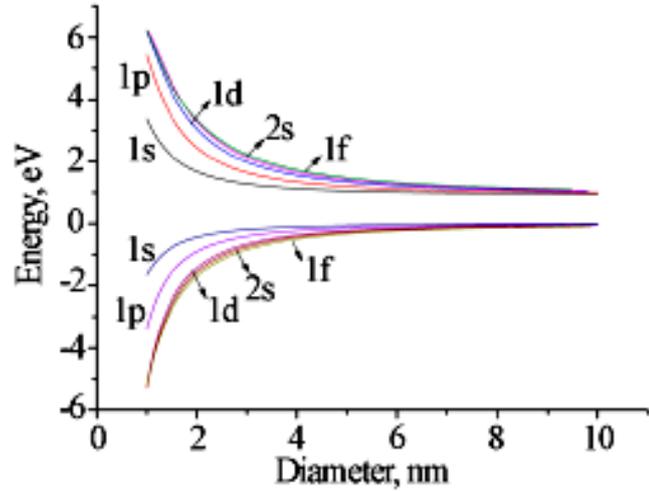
Here σ is the surface tension of a massive sample; υ is the volume of one mole; R is the gas constant; T is the temperature. In [13], it is shown that with an accuracy of 3% the following is fulfilled:

$$\sigma = 0.7 \cdot 10^{-3} T_{\mathrm{m}}, \qquad (7)$$

where T_{m} is the melting point of the solid (K). The ratio is fulfilled for all metals and for other crystalline compounds. At $T = T_{\mathrm{m}}$ we get:

$$d(\mathrm{I}) = 0.17 \cdot 10^{-9} \upsilon. \qquad (8)$$

Equation (8) shows that the thickness of the surface layer d(I) is determined by one fundamental parameter - the molar (atomic) volume of the element ($\upsilon = M/\rho$, M is the molar mass (g/mol), ρ is the density (g/cm^3)), which periodically changes in accordance with the table D.I. Mendeleev. The d(II) layer extends approximately to the size d(II) $\approx$10d = d$_\infty$, where the bulk phase begins. Dimensional properties begin from this size. By nanomaterials it is customary to mean materials, the main structural elements of which do not exceed the nanotechnological boundary of ~ 100 nm, at least in one direction [17]. A number of researchers are of the opinion that the upper limit (maximum size of elements) for nanostructures should be associated with some critical characteristic parameter: the mean free path of carriers in transport phenomena, the size of domains / domain walls, the diameter of the Frank-Read loop for sliding dislocations, etc.. This means that the layer d(II) should contain many dimensional effects associated with optics, magnetism, and other physical properties according to Eq. (5). As an example, Fig. 8 shows the size dependence of the luminescence of lithium uranates [18].
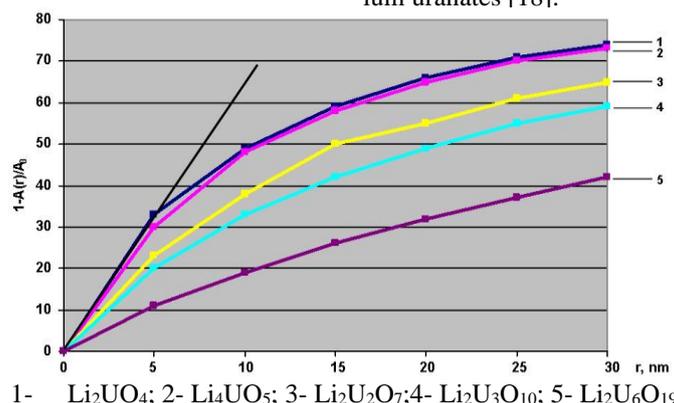

1-   Li$_2$UO$_4$; 2- Li$_4$UO$_5$; 3- Li$_2$U$_2$O$_7$;4- Li$_2$U$_3$O$_{10}$; 5- Li$_2$U$_6$O$_{19}$

Figure 8 - Dimensional dependence of luminescence of lithium urinates

Further research prospects are as follows

Our proposed multilevel model contains:

- de Broglie layer $d_0 = \lambda_{dB} = \hbar/p$ in which quantum size effects begin;

- layer d(I) defines "quasi-classical" size effects that are observed only in nanoparticles and nanostructures;

- layer d(II) contains many dimensional effects associated with optics (luminescence), magnetism, and other physical properties according to equation (2).

In the near future, detailed theoretical and experimental studies of the proposed multilevel model of nanostructured states in solids are urgently needed.

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