Electron-hole pairs multiquantum generation mechanism in the process of excitation of ZnSCdS – Cu by an atomic hydrogen

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Abstract
The luminescence of ZnSCdS – Cu phosphors of various CdS concentration (0 – 40%) is under investigation. The luminescence was exited by hydrogen atoms during adsorption of thermal energy during adsorption and impact recombination-heterogeneous chemiluminescence (HCL) are discussed. The monotone lowering of the conductivity zone bottom level with respect to the valence zone ceiling (from 3,7 eV to 3,2 eV) with increasing CdS concentration (from 0 – 40%). HCL intensity with respect to CdS (from 3,7 eV to 3,2 eV) concentration (Eg) grows rapidly. The dependence of HCL intensity on the forbidden zone width can be explained by the action of electron - hole pairs multiquantum generation mechanism.
The role of the crystal electron states in the energy accommodation process taking place in the gas-surface interaction is widely observed during luminescence of solids located into the active gas medium (free atoms, radicals). This kind of nonequilibrium luminescence is known to be called heterogeneous chemiluminescence \( HCL \) \cite{5}. Two modifications of \( HCL \) are known: radical-recombination and adsorption luminescence (\( RRL \) and \( AL \)) \cite{5} – \cite{7}. \( RRL \) is observed in the free atoms recombination process, \( AL \) - in the process of adsorption.

This paper presents the experimental results of \( RRL \) of \( ZnSCdS-Cu \) with the various concentrations of \( CdS(0 – 40\%) \), in the atomic hydride medium. The atomic hydride is produced by dissociation of the molecular hydride during high-frequency nonelectrode electric charge. In its turn, the molecular hydride is produced by diffusion through a heated palladium.

Kinetic, temperature and spectral characteristic of luminescence are studied with the help of photoelectric amplifier (\( PEA – 84 \)) attached to the output of a high-aperture monochromator, sometimes the interference filters are used.

In Fig.1, position of spectrum maxima of photo and heterogeneous chemiluminescence and the widths of forbidden zone \( E_g = E_g(ZnS)[1 – C(CdS)] + E_g(CdS)C(CdS) \) of phosphor \( ZnSCdS – Cu \) are given as functions of concentration of \( CdS(C(CdS) = 0 – 40\%) \). If can be noted that the rate of spectrum maxima and \( E_g(C) \) displaysments are practically the same. \( HCL \)
intensity with respect to $CdS$ - concentration ($E_g$ decreases) grows rapidly (Fig. 2).

For the $ZnSCdS - Cu$ phosphor containing the variable quantities of $CdS(0 - 40\%)$ it is established the $Cu^{2+}$-centre radiation spectrum is displaced to long wavelength (from 2.4$eV$ to 1.9$eV$). It is caused by monotone lowering of the conductivity zone bottom level with respect to the valence zone ceiling (from 3.7$eV$ to 3.2$eV$), position of the $Cu^{2+}$ - centre with respect to the valence zone ceiling being the same (theory of indirect activation [5]).

The dependence of the RRL intensity of the $ZnSCdS - Cu$ phosphor on the $CdS$ concentration can be explained by the action of electron-hole pairs multiquantum generation mechanism.

Because of the oscillation unharmonism and dependence of the dipole (quadrupole) momentum from binding on the internuclear coordinates, the interaction between the oscillotory excited dipole and the crystall electron states leads to transmission of several oscillatory quanta to electrons states at the same time.

If the Morze potential is chosen to describe the unharmonic oscillator, then the rate of the multiquantum oscillatory electron transitions by the zone-zone excitations can be expressed [4] as follows

\[ \Gamma_{ev} = \frac{4m_\theta^2f(m_r\hbar\omega_0)^{1/2}}{h\omega_0 Mm_e E_g} \left[ \frac{\mu(r_0)e(\varepsilon + 2)}{3a^{5/2}\varepsilon} \right]^2 \psi(q/E_g)e^{\exp(-E_g/h\omega_0)P}. \]  

(1)

Here: $m_e$ - mass of electron, $e$ - elementary electrical charge, $\omega_0 = \alpha(2q/m)^{1/2}$ - oscillator’s cyclic frequency, $\mu$ - dipole moment of binding, $f$ - oscillatory force, $\varepsilon$ - permittivity, corresponding to the transmission frequency, $q$ - adsorption potential depth, $E_g$ - width of forbidden zone, $m_r$ - equivalent effective mass of an electron - hole pair, $a$ - minimal distance of the energy transportation.

\[ \psi(x) = x^2(1 - x^{-1/2})(1 + 2x)^{-1/2} \]  

(2)

\[ p = z \ln z/(z - 1), z = (4q + \hbar\omega_0)/(E_g + \hbar\omega_0). \]  

(3)

(1) describes the oscillatory electron transition (inside the static region of a dipole) produced by the dipole interaction of a valence zone electron with the electromagnetic field of an unharmonic oscillator. To describe the dipole - quadrupole interaction, it is necessary to change the expression inside the rectangle parentheseses by $[eD(r_0)/5a^{5/2}]^2$.

The (1) and (3) describing the exitation rate can be used to evaluate the dependence of the phosphor $ZnSCdS - Cu$ luminiscence intensity on the $CdS$ concentration (the width of the phosphor’s forbidden zone), (Fig.2). Intensity
of $RRL_H$ depends on the exitation cross-section \[4\] and is proportional to the rate of the nonequilibrium electron state generation:

$$I \sim \frac{\Gamma_{ev}}{(\Gamma_{ev} + \Gamma_v)(1 + \tau_\omega)}(j\sigma_2 N_1 B_{RRL} + j\sigma_1 N B_{AL}). \quad (4)$$

Here: $\sigma_1$-adsorption cross-section, $\sigma_2$ - recombination cross-section, $N, N_1$ - correspondingly concentration of $AL$ and $RPL$ excitation centres, $B_{AL}, B_{RRL}$ - quantum yield of luminescence outputs of $AL$ and $RRL$ exitation centres, $(1 + \tau_\omega)^{-1}$ - concentration extinguish factor, $\Gamma_v + \Gamma_{ev}$ - total relaxation rate, $j$ - atom flux density.

These quantities does not (or in a rather small degree) depend on the energy width $E_g$.

For this situations according $(1 - 4)$ we get:

$$I_c = a/E_g \Psi(q/E_g) \exp(-E_g/\hbar\omega_0) \quad (5)$$

$$E_g = [3, 6 - 1, 1C(CdS)] eV \quad (6)$$

where $C(CdS)$ concentration $CdS$ inside the $ZnSCdS - Cu$ phosphor.

The theoretical curve $I(C)$ coincides (in the limits of experimental errors) with the experimental results (see Fig.2).$(\hbar\omega_0 = 0, 32 eV, q = 4 eV)$. The increment of $I(C)$ is not exponential and depends strongly on the factor $(1/E_g)\Psi(q/E_g)$.

When the $CdS$ concentration is great ($C > 60\%$), the $HCL$ output and intensity tend to be lower. It is caused by increasing of the concentration extinguish (factor $(1 + \tau_\omega)^{-1}$) and rate of the low - energy relaxation $\Gamma_v$ of the oscillatory exitation binding $(H - Me^{2+})^e - SU, (H - H)^e - SU$.

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