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Release of Electrons from Traps by an Electric Field with Phonon Participation

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The flash intensity of the ZnS–Cu phosphor induced by external dc field applied after excitation with ultraviolet light (Gudden-Pohl effect) is investigated. A method is used, which enables to study the temperature dependence of flash intensity for different applied voltages conditioned by centres of certain depth. The results are compared with the electron tunneling probability from the centre to the conduction band under phonon participation obtained in the paper.

Исследовались вспышки люминесценции, получаемые при наложении электрического поля на возбужденный ультрафиолетовым светом ZnS–Cu люминофор (эффект Гуддена-Поля). Применялась методика, позволяющая изучить температурную зависимость эффекта, обусловленного центрами определенной глубины, при различных напряжениях приложенного поля. Результаты сравниваются с вероятностью туннелирования электронов с участием фононов из центра в зону проводимости, полученной в настоящей работе.

1. Introduction

The theory of transitions of a valence electron into the conduction band in a semiconductor in a high electric field, taking into account electron–phonon interaction, was developed by Keldysh [1]. According to this theory the number of electrons per unit volume, which get into the conduction band per unit time with participation of one phonon may be calculated. The approximate formula of the diffusion of a valence electron into the conduction band with the absorption of several phonons was also presented.

In [2] in experiment the transition involving a phonon during investigations using an electroluminescence cell was, apparently, observed for the first time. In [3] multiphonon processes were established while measuring the temperature dependence of the Gudden-Pohl effect (GPE). From the study of the reduction of thermoluminescence peaks the deexcitation of a crystal by an applied electric field at room temperature was proved [4] to occur by tunneling with phonon participation. The trap ionization mechanism in a wide temperature range on the basis of the temperature dependence of GPE was studied in [5]. In the region of low temperatures the experimental results were shown to be in good agreement with the one-phonon theory and optical longitudinal phonons of the crystal lattice to take part in the electron transition. The results were compared with the multiphonon theory in the region of room temperature. A systematic disagreement between theory and experimental results was found. Moreover, the formula of multiphonon processes was found to be valid in a very narrow region

of temperatures and in a limited region of electric field strengths. The theory merely dealing with the transition of a valence electron into the conduction band, while in fact, the GPE arises as a consequence of the ionization of filled electron traps by the external electric field after the excitation of the luminophor, there is some disagreement in the comparison of the theory with experimental results. The tunneling probability from the traps to the band with phonon participation may differ from that for the band–band transition.

The thermoelectric ionization of the centres is usually considered following the Frenkel theory [6]. According to this theory, however, the temperature dependence of the ionization probability for deep centres is very steep, and this does not conform with experimental data.

In this paper the transition probability of an electron from a centre into the conduction band with phonon participation has been evaluated. The dependence of this probability on temperature is compared with the experimental temperature dependence of GPE for ZnS–Cu phosphors in the range from liquid nitrogen to room temperature.

2. Theory

The motion of an electron will be considered in the isotropic mass m^* approximation. Suppose that the deep impurity level originates from a local potential $U(\boldsymbol{r})$ proportional to the Dirac δ function. So, the total Hamiltonian describing the motion of an electron in the electric field and taking into account the electron–phonon interaction, has the form

$$H = -\frac{\hbar^2}{2m^*}\,\Delta + U(\boldsymbol{r}) - eFx + \sum_{\boldsymbol{q}\nu} \hbar\omega_{\boldsymbol{q}\nu}\left(b^+_{\boldsymbol{q}\nu}b_{\boldsymbol{q}\nu} + \frac{1}{2}\right) + V(\boldsymbol{r}, \{\boldsymbol{q}\nu\})\,, \tag{1}$$

$$V(\boldsymbol{r}, \{\boldsymbol{q}\nu\}) = iN^{-1/2} \sum_{\boldsymbol{q}\nu} \alpha_\nu(\boldsymbol{q})\,[b^+_{\boldsymbol{q}\nu} \exp(-i\boldsymbol{q}\boldsymbol{r}) - b_{\boldsymbol{q}\nu} \exp(i\boldsymbol{q}\boldsymbol{r})]\,. \tag{2}$$

Here $\boldsymbol{r}$ denotes the electron radius vector, $V(\boldsymbol{r}, \{\boldsymbol{q}\nu\})$ is the electron–phonon interaction operator, e the electron charge, and F the electric field strength. $b^+_{\boldsymbol{q}\nu}$ and $b_{\boldsymbol{q}\nu}$ are the creation and annihilation operators of phonons with wave vector $\boldsymbol{q}$ and energy $\hbar\omega_{\boldsymbol{q}\nu}$ of the vibrational branch ν, N is the number of atoms in the crystal, and $\alpha_\nu(\boldsymbol{q})$ are the electron–phonon interaction constants.

The probability of the electron tunneling per unit time from the deep impurity level to the conduction band can be calculated using the conventional perturbation theory formula

$$W = \frac{2\pi}{\hbar}\,\mathrm{Av}\,\{n^0_{\boldsymbol{q}\nu}\} \sum_{E_1, \boldsymbol{k}, \{n_{\boldsymbol{q}\nu}\}_{E_1}} |\int \mathrm{d}\boldsymbol{r}\,\psi^*_{\boldsymbol{k}E_1}(\boldsymbol{r})\,eFx\varphi_0(\boldsymbol{r})|^2 \times$$

$$\times\, |\langle\{n_{\boldsymbol{q}\nu}\}_{E_1} \mid \{n^0_{\boldsymbol{q}\nu}\}\rangle|^2\, \delta\left[E_1 + \frac{\hbar^2k^2}{2m^*} + E(\{n_{\boldsymbol{q}\nu}\}_{E_1}) + \Delta_0 - E(\{n^0_{\boldsymbol{q}\nu}\})\right] \tag{3}$$

which can be expressed in the form

$$W = \int_{-\infty}^{\infty} W_0(\varepsilon)\, g(\varepsilon)\, \mathrm{d}\varepsilon\,, \tag{4}$$

$$W_0(\varepsilon) = \frac{2\pi}{\hbar} \sum_{E_1 \boldsymbol{k}} |\int \mathrm{d}\boldsymbol{r}\,\psi^*_{\boldsymbol{k}E_1}(\boldsymbol{r})\,eFx\varphi_0(\boldsymbol{r})|^2\, \delta\left(E_1 + \frac{\hbar^2k^2}{2m^*} + \Delta_0 - \varepsilon\right), \tag{5}$$

$$g(\varepsilon) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} \mathrm{d}t\ \mathrm{Av}\ \{n^0_{\boldsymbol{q}\nu}\} \sum_{\{n_{\boldsymbol{q}\nu}\}-\Delta_0} \exp\left[-\frac{i}{\hbar}\left(\varepsilon + E\left(\{n_{\boldsymbol{q}\nu}\}_{-\Delta_0}\right) - \right.\right.$$

$$\left.\left. - E(\{n^0_{\boldsymbol{q}\nu}\})\right) t\right] |\langle \{n_{\boldsymbol{q}\nu}\}_{-\Delta_0} | \{n^0_{\boldsymbol{q}\nu}\}\rangle|^2 . \tag{6}$$

Here $\varphi_0(\boldsymbol{r})$ is the wave function of the electron localized on the impurity centre and $\psi_{\boldsymbol{k}E_1}(\boldsymbol{r})$ the wave function describing the electron motion with the wave vector $\boldsymbol{k}$ perpendicular to the x-axis and with energy E_1 parallel to x in the conduction band in a strong electric field. Δ_0 is the ionization energy of the impurity centre and $\langle \{n_{\boldsymbol{q}\nu}\}_{-\Delta_0} | \{n^0_{\boldsymbol{q}\nu}\}\rangle$ the overlap integral of the phonon functions, calculated in the adiabatic approximation, of the initial $\{n^0_{\boldsymbol{q}\nu}\}$ and final $\{n_{\boldsymbol{q}\nu}\}_{-\Delta_0}$ states. $\mathrm{Av}\{n^0_{\boldsymbol{q}\nu}\}$ denotes the averaging over the distribution of phonons in the initial state. In deriving (4 to 6) we assumed that $|\{n_{\boldsymbol{q}\nu}\}_{E_1}\rangle \approx |\{n_{\boldsymbol{q}\nu}\}_{-\Delta_0}\rangle$.

From expressions (4 to 6) follows, that the total tunneling probability of an electron from the deep impurity level to the conduction band is proportional to the overlap integral (4) of the pure electronic tunneling probability (5) with the function $g(\varepsilon)$ (6). As we see, $g(\varepsilon)$ describes the shape of the impurity absorption band resulting from the electron–phonon interaction.

As it was shown in [7] by one of the authors of this paper, the pure electronic tunneling probability $W_0(\varepsilon)$ in a strong electric field can be expressed in the form

$$W_0(\varepsilon) = \frac{eF}{2(2m^*\Delta)^{1/2}} \exp\left[-\frac{4}{3}\frac{(2m^*)^{1/2}(\Delta - \varepsilon)^{3/2}}{eF\hbar}\right], \tag{7}$$

where $\Delta \approx \Delta_0$. This expression has a similar form as that obtained by Franz [8] in a different way.

It is well known that the shape of the absorption band for strong electron-phonon interaction can be approximated by a Gauss function [9 to 11]. Hence, the total tunneling probability W can be expressed in the form

$$W = \frac{eF}{2(2m^*\Delta)^{1/2}} \frac{2}{\pi^{1/2}\Gamma}\int_{-\infty}^{\Delta} \mathrm{d}\varepsilon \exp\left[-\frac{4}{3}\frac{(2m^*)^{1/2}(\Delta-\varepsilon)^{3/2}}{eF\hbar} - \frac{4\varepsilon^2}{\Gamma^2}\right], \tag{8}$$

where Γ is the width of the impurity absorption band. When the electron interacts predominantly with the longitudinal optical phonons, the width Γ depends on temperature as given in [11]

$$\Gamma^2 = \Gamma_0^2(2\bar{N}_k + 1), \quad \bar{N}_k = \left[\exp\frac{\hbar\omega_0}{kT} - 1\right]^{-1}, \tag{9}$$

where $\hbar\omega_0$ is the phonon energy.

Since the exponent in (8) contains a very large number, we can use the saddle-point method to evaluate the integral, whence we get

$$W = \frac{\omega_0}{\alpha}\left[(1+\gamma^2)^{1/2} - \gamma\right]^{1/2}\left[1+\gamma^2\right]^{-1/4} \exp\left\{-\frac{2}{3}\alpha\frac{\Delta}{\hbar\omega_0}\times\right.$$

$$\left.\times\left[(1+\gamma^2)^{1/2} - \gamma\right]^2\left[(1+\gamma^2)^{1/2} + \frac{1}{2}\gamma\right]\right\}, \tag{10}$$

where

$$\alpha = \frac{2(2m^*\Delta)^{1/2}\,\hbar\omega_0}{eF\hbar}; \quad \gamma = \alpha\,\frac{\Gamma^2}{16\hbar\omega_0\Delta}. \tag{11}$$

Expression (10) differs significantly from the electron tunneling probability from the valence band to the conduction band developed by Keldysh [1], taking into account the one-phonon absorption and emission processes:

$$W_0 \sim \left\{\bar{N}_k + (1+\bar{N}_k)\exp\left[-\frac{4(2m^*\Delta)^{1/2}}{eF\hbar}\,\hbar\omega_0\right]\right\} \times$$
$$\times \exp\left[-\frac{4}{3}\,\frac{(2m^*)^{1/2}}{eF\hbar}\,(\Delta-\hbar\omega_0)^{3/2}\right], \tag{12}$$

where Δ is the width of the forbidden band.

3. Experimental Results and their Comparison with Theory

The powder of ZnS–Cu (10^{-5} g/g) phosphor with sphalerite-type structure had been prepared by heating at 900 °C in air with 3% NaCl. The sample under investigation was a cell with the phosphor layer, with a plate of mica placed between the transparent electrode and the phosphor layer.

The temperature dependence of GPE of a particular centre was measured after excitation of the sample at a temperature T_Δ by which the investigated and deeper centres had been filled. After excitation the sample was cooled in darkness to the temperature at which the dc electric field was switched on, and the GPE flash intensity was measured. In order to avoid after-effects of a previous voltage application the sample was irradiated by infrared light for a time of 5 min. In the following measurements after sample excitation at the same temperature T_Δ the electric field was applied at another temperature. In order to investigate the GPE from other centres, the excitation of the sample was carried out at other temperatures $T_{\Delta'}$.

The sample was mounted in a vacuum cryostat during experiments. By means of a monochromator the mercury line 365 nm was selected for the excitation. For light intensity measurements photomultiplier and dc amplifier with recorder or galvanometer were used.

The investigated sample had a complicated energy spectrum of traps. The thermoluminescence curve is represented in Fig. 1. For the determination of trap depths the initial-rise method of thermal glow curves was used. The GPE

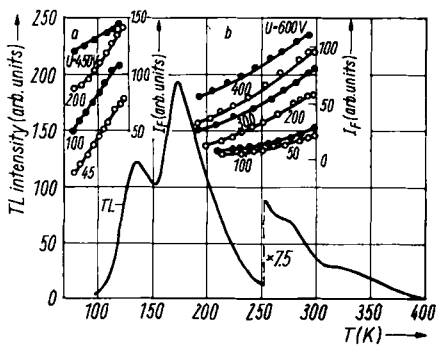

Fig. 1. Thermal glow curve (TL) for a ZnS–Cu (10^{-5} gCu/gZnS) phosphor after excitation at 80 K with the mercury line 365 nm. Heating rate 0.07 K s^{-1}. a) Decrease of the flash intensity I_F with diminution of temperature at various applied fields. Excitation at 130 K. b) The same as in Fig. 1a after excitation at 310 K

was investigated for the traps with energy depths 0.2, 0.42, 0.52, 0.56, 0.64 eV. The temperature dependence of GPE (in arbitrary units) is shown in Fig. 1a for the 0.2 eV and in Fig. 1b for the 0.64 eV trap depths.

On the basis of the fact that the GPE is due to the release of electrons from traps by the electric field and succeding their radiative recombination with centres, the GPE flash intensity can be proportional to the electron release probability. This is the case when the concentration of trapped electrons is the same for the whole series of measurements and if their radiative recombination prob-

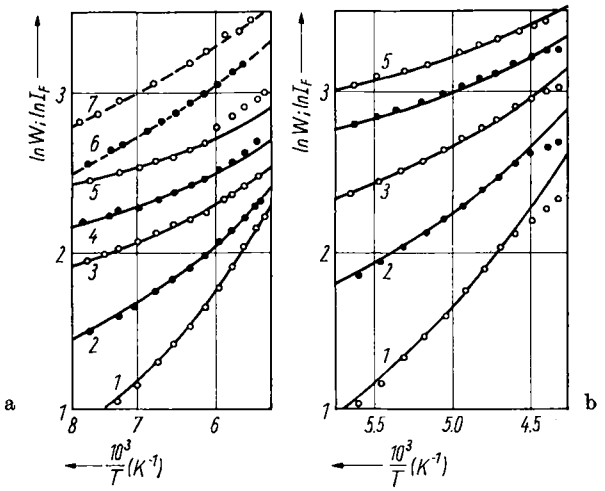

Fig. 2. a) The dependence of ln W for 0.42 eV traps (lines) and of the logarithm of flash intensity (points) after excitation at 130 K upon $1/T$. The values of field strength for theoretical curves and applied voltage are presented in Table 1. b) The same as in Fig. 2a for 0.52 eV; excitation at 243 K

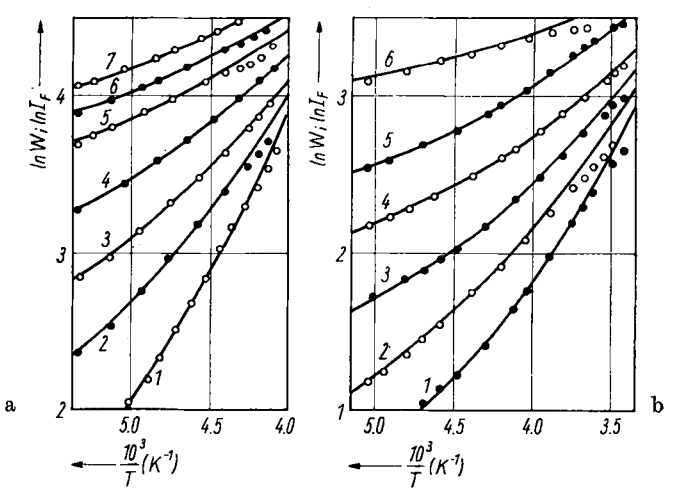

Fig. 3. The same as in Fig. 2. a) for $\Delta = 0.56$ eV, excitation at 273 K, b) for $\Delta = 0.64$ eV, excitation at 310 K

Table 1

curve	Fig. 2a			Fig. 2b			Fig. 3a			Fig. 3b			Fig. 4		
	U (V)	F (10^7 V/m)	$\frac{F}{\sqrt{U}} \times 10^{-6}$	U (V)	F (10^7 V/m)	$\frac{F}{\sqrt{U}} \times 10^{-6}$	U (V)	F (10^7 V/m)	$\frac{F}{\sqrt{U}} \times 10^{-6}$	U (V)	F (10^7 V/m)	$\frac{F}{\sqrt{U}} \times 10^{-6}$	U (V)	F (10^7 V/m)	$\frac{F}{\sqrt{U}} \times 10^{-6}$
1	45	2.7 ± 0.2	4.2	60	3.6 ± 0.1	4.7	30	2.7 ± 0.2	4.9	50	4.7 ± 0.1	6.6	45	$\leqslant 3$	4.5
2	60	3.7 ± 0.1	4.8	150	5.0 ± 0.1	4.1	60	4.0 ± 0.1	5.2	100	6.0 ± 0.1	6.0	100	5.2 ± 0.1	5.2
3	100	5.5 ± 0.1	5.5	300	6.8 ± 0.1	3.9	90	5.0 ± 0.1	5.3	200	6.8 ± 0.1	4.8	200	6.4 ± 0.1	4.5
4	150	6.0 ± 0.1	4.9	450	8.5 ± 0.1	4.0	150	6.0 ± 0.1	4.9	300	8.3 ± 0.1	4.8	450	10 ± 0.2	4.7
5	200	6.5 ± 0.1	4.6	600	9.5 ± 0.2	3.9	300	7.5 ± 0.1	4.3	400	8.8 ± 0.2	4.4			
6	400						450	8.0 ± 0.1	3.8	600	11 ± 0.5	4.5			
7	600						600	8.5 ± 0.1	3.5						

ability is constant (or changes only slightly) in the investigated region of temperatures. Consequently, the temperature dependence of the probability calculated from formula (10) can be compared with the temperature dependence of GPE.

By means of a computer the dependence of ln W on temperature was calculated for a set of experimentally determined trap depths and for different Γ_0 values. The following values of parameters were used: $m^* = 0.39 m_e$ [12], $\hbar\omega_0 = 0.043$ eV [13]. The calculated curves were compared with the temperature dependence of GPE. The best coincidence was found for the parameter $\Gamma_0 = 4\hbar\omega_0$. The comparison of results for centres $\Delta = 0.42$, 0.52, 0.56, and 0.64 eV is given in Fig. 2 and 3.

It is seen from Table 1 that the electric field strengths obtained by comparison of theoretical curves with experimental results for different trap depths but for the same applied voltage are approximately equal. The comparison of theory with experimental data for the trap 0.2 eV gives electric field strengths three times less than those obtained for deeper centres. It follows that the theory of tunneling from the centres is inadequate for these traps. In this case, the disagreement with experiment appears to be not only quantitative but also qualitative. Indeed, when the applied electric field strengths are decreased the slope of ln I_F curves has the tendency to reach the limit. Such a behaviour of curves follows from the one-phonon theory [1] and on this basis in [5] the energy of a phonon which takes part in the tunneling process was established.

In Fig. 4 the comparison of the temperature dependence of GPE for the 0.2 eV trap depth with the theory of the one-phonon transition is shown. In this case, we have the same electric field strengths as from multi-phonon theory (10) for the deeper centres. The coincidence of one-phonon theory with the experimental results on GPE indicates that

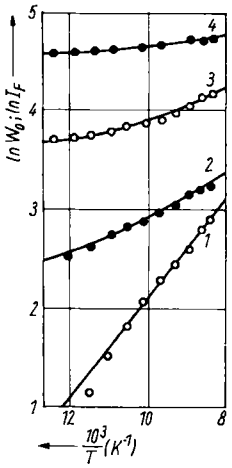

Fig. 4. The dependence of ln W_0 for 0.2 eV traps (lines) and ln I_F (points) upon $1/T$. Excitation at 130 K

shallow traps apparrently form an impurity band in this case.

Moreover, a definite regularity was observed between the applied voltages and electric field strengths determined from the curves. The ratio of field strength to square root of applied voltage was proved to be approximately the same for corresponding curves (see Table 1). Proportionality of the field strength to the square root of applied voltage indicates that the centre ionization occurs in the Mott-Schottky exhaustion barrier.

The ratio $F/\sqrt{U}$ only slightly decreases for higher applied voltages. This may be caused either by noticeable changes of the absorption band width in a strong field (Γ_0 increases) or by the influence of deeper traps.

Another disagreement of theory with experiment for the 0.42 eV centre (see Fig. 2a) is to be mentioned briefly. The slope of the curves in the higher temperature region begins to rise when the applied voltage is increased (curves 4 to 7). The reason for this phenomenon can be that for higher applied voltage the release of electrons from deeper centres gives a noticeable contribution to the flash intensity.

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