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Dose dependences of phosphorescence and conduction current relaxation in single crystals of Zinc Selenide

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At the excitation temperature, at least three types of traps (shallow, phosphorescent and deep) are involved in the processes of phosphorescence and relaxation of the conduction current. This necessitates the use of a crystal phosphorus multicenter model for which a theoretical dependence for between the intensity of phosphorescence and relaxation of the conduction current has been obtained. These dependences take into account the re-trapping of free charge carriers on shallower traps. The traps filling level depend not only on the total radiation dose but also on the intensity of excitation. For the doses of X-ray irradiation varying within four orders of magnitude, all experimental dependences of the intensity of phosphorescence and relaxation of the conduction current for ZnSe crystals are well described by the obtained theoretical dependences. The dose dependences of phosphorescence and conduction current relaxation which were obtained concurrently from different samples confirm that the trap release time for each type of the trap is determined not only by the probability of the thermal release of charge carriers from the traps, but also by the ratio of the concentration of an individual trap to the total concentration of the deeper traps.

Keywords: luminescence, conductivity, phosphorescence, conduction current relaxation, X-ray excitation, ZnSe crystals.

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Introduction

The phosphorescence phenomenon has been known for a long time and is often described by Becquerel's phenomenological formula, first proposed more than 100 years ago. And yet, over a hundred years on, there are no documented theoretical dependences for phosphorescence intensity (Ph) and conduction current relaxation (RC), which are functionally close to each other, but not similar for a wide dynamic range of excitations. And this is so despite the fact that these processes are observed in all wide-band semiconductors and dielectrics. Certain theoretical dependences describing the relaxation processes after the cessation of excitation were obtained [1, 2] for the crystal phosphor multicenter model using the kinetic theory framework of luminescence and conductivity.

It is convenient to use zinc selenide (ZnSe) monocrystals as model crystal phosphors for the construction and experimental verification of the general kinetic theory of luminescence and conductivity. High-resistance ZnSe crystals have sufficiently intense steady-state luminescence, Ph, thermally luminescence, and steady-state conduction current, RC, thermally stimulated conductivity under X-ray excitation, which allows simultaneous measurement of luminescence and conductivity. ZnSe belongs to wide-gap materials of type $A^{II}B^{VI}$ [3-8] and is used in the creation of semiconductor electronic devices and information display systems. Over the last decade, another promising area of application of ZnSe has emerged – that of detectors of indirect ionizing radiation [4-7] and direct energy conversion of high-energy radiation into electric current [8]. The use of undoped ZnSe as a semiconductor detector became possible only after the development of technologies for growing high-quality monocrystals with low concentrations of uncontrolled impurities and high resistivity at ~10^{10}÷10^{14} Om·sm.

Looking at just the phosphorescence curve or relaxation curve of the conduction current, one could only conclude that the material is accumulating light, but it is practically impossible to obtain any reliable characteristics of the material itself. In order to obtain these characteristics, it is necessary to register a series of Ph and RC curves at different doses of irradiation and establish theoretical dependences for them. Therefore, the aim of the study was to determine, from the dose dependences of Ph and RC obtained at different intensities of X-ray excitation, the parameters of the centers that cause long-term phosphorescence and relaxation of the conduction current.

I. Experimental method

ZnSe crystals were grown from a pre-purified mixture and were left specifically undoped during the growth process. Indium electrical contacts in the form of two parallel strips (1×5 mm^2, i.e. L = 5 mm) were deposited on to monocrystal samples using the resistive method, to which copper conductors were soldered.

X-ray radiation was used to accumulate light. The surface of the sample between the electrical contacts was irradiated with the integral radiation of the BHV-7 X-ray tube (Re, 20 kV, 25 mA (I_{X1} = 0.64 nW/sm^2) or 5 мmA (I_{X2} = 0.13 mW/sm^2), L = 130 mm) through a beryllium window of the cryostat. The dose dependences of Ph and RC were measured simultaneously after X-ray irradiation for a fixed time period τ_x at a temperature of 85 K. Two channels were used to record the luminescence of the sample: integral and spectral. The optical axes of the two registration systems passed exactly through the middle between the two electrical contacts and at a 45° angle to the sample plane normal which was uniformly irradiated. The accuracy of determining the intensity of the glow was not worse than 5% and was limited by the presence of dark currents of the photomultiplier tube and by the registration system noises.

II. Theoretical dependences of phosphorescence and relaxation current

It has long been known that Ph and RC observed in crystals after UV or X-ray excitation are due to the delocalization of charge carriers into the trap zone and recombination with recharged luminescence centers. It is known that the spectral composition of phosphorescence and thermally stimulated luminescence (TSL) in ZnSe coincides with the spectra of photo- and X-ray luminescence [9]. The spectrum is dominated by two recombination luminescence bands with maxima at 630 nm (1.92 eV) and 970 nm (1.28 eV) [9]. The 630 nm band, according to [10, 11], is determined by a complex center that includes a zinc vacancy, and the band with a maximum at 970 nm is caused by a complex center with a selenium vacancy [12, 13]. Both luminescence bands are due to the recombination mechanism of luminescence, as they are observed in Ph and TSL curves [14].

Ph and RC curves were measured for two ZnSe samples at two intensities of X-ray excitation after different doses of irradiation (10 doses each). Figure 1 shows two such series of twelve measurements.

A characteristic feature for all series of measurements is: 1) an increase in intensity, 2) the presence of saturation of the curves, 3) a decrease in the decay rate with an increase in the radiation dose and for the decay of Ph and RC.

The theoretical dependences of Ph and RC intensities for the crystal phosphorus multicenter model [1] were calculated in [2] and the formula was obtained as a sum of three exponents. At the same time, it was taken into account that all instances of delocalization of electrons from traps and their subsequent localization or recombination are independent processes. Each exponent is attributable to the delocalization of charge carriers from a shallow, phosphorescent, and deep trap. The exponent time constants are determined not only by

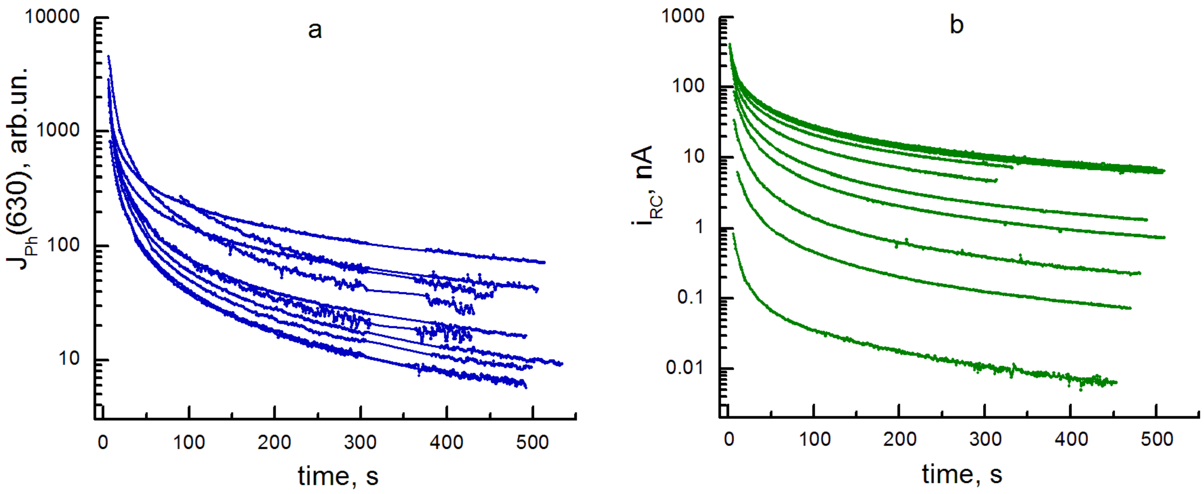

Fig. 1. Attenuation of phosphorescence in the 630 nm band (a) and relaxation of conduction current (b) in ZnSe sample #1, at T = 85 K, and after different times of X-ray irradiation (I_{X2}): 5 s; 12 s; 24 s; 1 min; 2 min; 5 min; 10 min; 25 min; 1 h; 2 h.

the life time of the carriers in the trap, but also depend on the ratio of the concentrations of this trap to the concentration of a deeper trap. The study in [1] then took into account the change in the concentration of recharged luminescence centers in which the recombination of charge carriers delocalized from traps occurs and an additional factor appears in each of the exponents. In many crystals, the concentration of shallow traps (ν_s) is greater than the concentration of phosphorescent (ν_{ph}) and deep traps ($\nu_{d1}+\nu_{d2}$), which is observed in the TSL and TSC curves post different excitation temperatures. Therefore, both during excitation and post excitation, a free electron can be localized on shallow traps dozens of times before its recombination or localization on a deep trap, or until it hits an electrical contact. The statistics of intermediate electron localizations on shallow traps will be described by the Poisson distribution: $P_k = \frac{m_s^k}{k!}\exp(-m_s)$, where k is the number of acts of intermediate electron localizations on shallow traps, and m_s is the average number of acts of intermediate localizations. Taking into account the processes of re-trapping [15] gives the corresponding theoretical dependences for the values of RC and Ph:

$$i_{RC}(t) = i_{0s}\sum_{k=0}^{k_{max}}\frac{m_s^k\exp(-m_s)}{k!}\exp(-t/(k+1)\tau_s) + \frac{i_{0ph}}{\left(1/\tau_{ph}^* - 1/(m_s+1)\tau_s\right)}\left(\frac{\exp(-t/\tau_{ph}^*)-\exp(-t/(m_s+1)\tau_s)}{1+r_{ph}m_{ph}\left[1-\exp\left(-t/\tau_{ph}^*\right)\right]}\right) + \frac{i_{0d}}{\left(1/\tau_{d1}^*-1/\tau_{ph}^*\right)}\left(\frac{\exp(-t/\tau_{d1}^*)-\exp(-t/\tau_{ph}^*)}{1+r_{d1}m_{d1}[1-\exp(-t/\tau_{d1}^*)]}\right) \quad (1)$$

$$J_{ph} = J_{0s}\cdot\sum_{k=0}^{k_{max}}\frac{m_s^k\exp(-m_s)}{k!}\exp(-t/(k+1)\tau_s) + \frac{J_{0ph}}{\left(1/\tau_{ph}^*-1/(m_s+1)\tau_s\right)}\frac{\exp(-t/\tau_{ph}^*)-\exp(-t/(m_s+1)\tau_s)}{\left\{1+r_{ph}m_{ph}\left[1-\exp\left(-t/\tau_{ph}^*\right)\right]\right\}^{\left(1+\frac{\sigma_p^-}{\sigma_{ph}^-}\right)}} + + \frac{J_{0d1}}{\left(1/\tau_{d1}^*-1/\tau_{ph}^*\right)}\frac{\exp(-t/\tau_{d1}^*)-\exp(-t/\tau_{ph}^*)}{\{1+r_{d1}m_{d1}[1-\exp(-t/\tau_{d1}^*)]\}^{\left(1+\frac{\sigma_p^-}{\sigma_{d1}^-}\right)}} \quad (2)$$

where: i_{0s}, i_{0ph}, i_{0d} – the initial value of the relaxation current during the release of carriers from shallow, phosphorescent, and deep traps; J_{0s}, J_{0ph}, J_{0d} – initial Ph intensities during carrier delocalization from shallow, phosphorescent, and deep traps; τ_s, τ_{ph}, τ_{d1} – lifetime of free charge carriers in shallow, phosphorescent and deep traps; τ_{ph}^*, τ_{d1}^* – phosphorescent and deep trap release time ($\tau_{ph}^* = \tau_{ph}\times(1+m_{ph})$, $\tau_{d1}^* = \tau_{d1}\times(1+m_{d1})$); m_{ph}, m_{d1} – average number of acts of intermediate localizations on phosphorescent and deep traps; r_{ph}, r_{d1} – filling levels of the phosphorescent and deep traps; σ_p^-/σ_{ph}^- – the ratio of free carrier localization cross sections to luminescence and trap centers.

These theoretical dependences were compared with experimental data and the parameters of the theoretical dependences were selected so that the deviation was minimal. For two ZnSe monocrystal samples and two X-ray excitation intensities, theoretical dependences were selected so that the standard deviation of the theoretical curves from the experimental ones was minimal [16]. For all relaxation curves of the conduction current (U_0 = 15 V) and phosphorescence (for the bands of 630 and 970 nm), a good approximation of the experimental curves by theoretical ones is observed. Note that the Ph (J_{630}, J_{970}) and RC (i_{RC}) curves were recorded simultaneously. A comparison of the characteristics shows that practically the same values are observed for all the curves of Ph and RC τ_s = 0.35 s, τ_{ph} = 7 s, τ_{d1} = 150 s. The m parameters remain the same for the first sample, but different for the second; respectively, for #1: m_s = 14, m_{ph} = 7, m_{d1} = 1.5; for the second sample #2: m_s = 16, m_{ph} = 12, m_{d1} = 10. It is clear that the filling of each trap increases with increasing X-ray radiation dose.

Having all the parameters of all theoretical dependences, it is possible to determine or estimate the main characteristics of the local centers that correspond to Ph and RC.

Conclusions

Studies of phosphorescence and conduction current relaxation, which were recorded simultaneously on undoped high-resistance ZnSe crystals of high optical quality, showed that these two processes are caused by the delocalization of charge carriers from almost all traps. Moreover, during the relaxation process, intermediate localization of charge carriers on the traps is observed. The analytically obtained theoretical dependences for Ph and RC, which take into account the intermediate acts of localization of charge carriers on shallower traps. It was established that at the excitation temperature, at least three types of traps (shallow, phosphorescent, and deep) are involved in Ph and RC. All experimentally obtained curves are well described by theoretical dependences.

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Дозові залежності фосфоресценції та релаксації струму провідності в кристалах ZnSe.

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При температурі збудження в процесах фосфоресценції та релаксації струму провідності приймають участь як мінімум три типи пасток (мілка, фосфоресцентна та глибока). Тому необхідно використовувати багатоцентрову модель кристалофосфору, для якої одержані теоретичні залежності інтенсивності фосфоресценції і релаксації струму провідності. Ці залежності враховують процеси повторної локалізації носіїв заряду на усі пастки. Рівень заповнення різних пасток залежить від інтенсивності збудження, а не тільки від загальної дози опромінення. Усі експериментальні залежності інтенсивності фосфоресценції і релаксації струму провідності для кристалів ZnSe (дози рентгенівського опромінення змінювались в межах чотирьох порядків) добре описуються одержаними теоретичними залежностями. Одержані одночасно дозові залежності фосфоресценції і релаксації струму провідності в різних зразках підтверджують, що час спустошення кожного типу пасток визначається не тільки імовірністю термічної делокалізації, а й співвідношенням концентрації цієї пастки до загальної концентрації більш глибоких пасток.

Ключові слова: люмінесценція, провідність, фосфоресценція, релаксація струму провідності, рентгенівське збудження, кристали ZnSe.