

# Kinetics of the luminescence decay of Fe<sup>2+</sup> impurity centres in polycrystalline ZnSe upon excitation by an electron beam

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**Abstract.** The kinetics of the decay of the luminescence of Fe<sup>2+</sup> ions is measured at nitrogen temperature in polycrystalline ZnSe excited by a short pulse of accelerated electrons. The time dependence of the luminescence intensity differs from the exponential one, observed upon excitation of luminescence by a short light pulse. The obtained nonexponential dependence is theoretically described. The explanation is based on the quenching effect of the excited state of the Fe<sup>2+</sup> ion by free electrons of the volume charge of the current of accelerated electrons in the sample (Auger effect). It was shown that the relaxation of the volume charge after the electron-accelerating voltage is removed makes a significant contribution to the decay kinetics of the impurity luminescence.

**Keywords:** Auger effect, ZnSe:Fe<sup>2+</sup> crystal, electron-impact excitation of luminescence.

## 1. Introduction

A ZnSe:Fe<sup>2+</sup> crystal is one of the active materials of solid-state lasers emitting in the spectral range of 4–5 μm [1–4]. At present, lasers based on this material, as well as all lasers with active elements based on solid-state materials with impurity centres, are pumped by optical radiation. However, work is underway to excite impurity centres in this material by electron impact. In [5], luminescence of the Fe<sup>2+</sup> ion in ZnSe was measured upon excitation by a short pulse of accelerated electrons. In addition to Fe<sup>2+</sup>, other ferrous and ferric ions of the iron group, for example Cr<sup>2+</sup>, are also embedded into the ZnSe crystal, and there are a number of works examining the electron-impact excitation of the Cr<sup>2+</sup> ion. Without dwelling on a detailed review of works related to the study of ZnSe:Cr<sup>2+</sup>, we single out a relatively recent work [6], where luminescence of the Cr<sup>2+</sup> ion was observed in a ZnSe crystal additionally doped with aluminium ions when a current flows through it.

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The kinetics of the luminescence decay of excited Fe<sup>2+</sup> ions at low temperature, observed in [5], is complex and there is no explanation of the time dependence of the luminescence intensity of these centres.

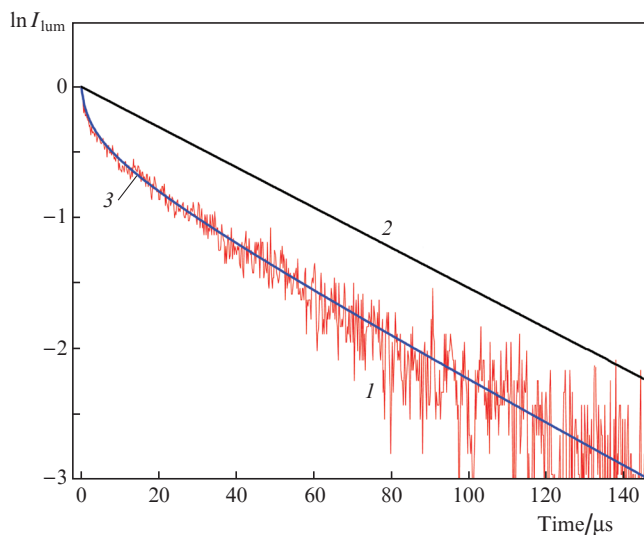
In this paper, we have measured the kinetics of the luminescence decay of Fe<sup>2+</sup> ions in polycrystalline CVD-ZnSe excited by a short pulse of accelerated electrons at nitrogen temperature. In contrast to [5], where a ZnSe single crystal was used, we have examined a CVD-ZnSe polycrystal. Structurally, the ZnSe:Fe<sup>2+</sup> single crystal and CVD-ZnSe:Fe<sup>2+</sup> are different materials. The observed kinetics of luminescence decay is explained.

## 2. Experimental

As an initial material, we used a ZnSe crystal synthesised by chemical vapour deposition (CVD-ZnSe). The ZnSe:Fe<sup>2+</sup> sample was made in the form of a disk with a diameter of 20 mm and a thickness of 4 mm. The synthesis procedure was as follows. An iron film was electron-beam deposited in vacuum on one of the polished surfaces of two ZnSe disks. The film thickness was ~1 μm. Disks with an iron film were placed in a quartz ampoule filled with argon, sealed in it, and annealed at a temperature of 1000 °C for 60 h to dissolve the film and diffuse iron into the bulk of the samples. Then the disks were polished and assembled so that their doped surfaces were in contact with each other. The resulting assembly was installed in a graphite mold isolated from zinc selenide with a thermally expanded graphite foil. The mold with the sample was placed in a hot pressing unit, heated in vacuum to a temperature of 1000 °C and kept at a maximum temperature for 180 min with a uniaxial pressure of 25 MPa. As a result of this treatment, the disks were diffusion bonded with each other. Next, the sample was subjected to high-temperature gas-static treatment in argon for 28 hours at a pressure of 100 MPa and a temperature of 130 °C. A more detailed procedure for the fabrication of ZnSe samples with internal doping by iron is described in [7]. After completion of the bonding procedure, we obtained a ZnSe:Fe<sup>2+</sup>:ZnSe sample, which had the form of a disk, inside of which there was a flat Fe<sup>2+</sup>-doped region located perpendicular to the disk axis. Its thickness was ~2 mm. The disk was used as a blank from which a 2-mm-thick plane-parallel plate was cut so that the plate surfaces were parallel to the disk axis. In this case, the Fe<sup>2+</sup>-doped region emerged on the plate surface in the form of bands. These surfaces were polished. When the plate was irradiated, the electron beam acted on this region, as well as on neighbouring regions weakly doped with iron.

When luminescence of Fe<sup>2+</sup> ions is excited in a ZnSe crystal, accelerated electrons are incident on a crystal located on the anode of the electron gun and in ohmic contact with it. Luminescence was excited by an electron pulse of  $\sim 250$  ns duration with an accelerating voltage of  $\sim 40$  kV and a maximum current of 30–100 mA. The experimental technique is described in more detail in [5]. The luminescence radiation with a wavelength near 4000 nm was recorded.

Figure 1 shows the time dependence of the natural logarithm normalised to the maximum luminescence intensity of Fe<sup>2+</sup> ions at nitrogen temperature (curve 1). The linear dependence of  $f(t) = t/\tau_r$  is also presented for the lifetime  $\tau_r = 65$   $\mu$ s of the excited state of Fe<sup>2+</sup>, which corresponds to the exponential law of luminescence decay (curve 2). One can see that the experimental dependence in the initial section (immediately after the termination of the electron pulse action) differs markedly from the linear one and becomes close to it at times exceeding 50  $\mu$ s. These features of the luminescence kinetics are especially clearly seen when comparing curves 1 and 2.



**Figure 1.** (1) Time dependence of the natural logarithm of luminescence of Fe<sup>2+</sup> in ZnSe, normalised to maximum intensity  $I_{lum}$ ; (2) linear dependence corresponding to the exponential kinetics of luminescence decay; and (3) calculated curve.

### 3. Discussion of the results

It was shown in [8] that the additional doping of a ZnSe: Fe<sup>2+</sup> crystal with aluminium ions, which is a shallow donor, leads to the fact that the sample transmittance for radiation with a wavelength of 2940 nm is almost independent of its intensity (at an intensity less than 4.6 MW cm<sup>-2</sup>) both at room and low temperatures. The absence of a change in the sample transmittance for high-power radiation was explained in [8] by an increase in the saturation intensity of the transition for resonant radiation due to a decrease in the lifetime of the upper Fe<sup>2+</sup> level.

A decrease in the lifetime of the excited state of the Fe<sup>2+</sup> ion, in turn, was associated with the manifestation of the Auger effect of impurity luminescence quenching by free electrons (see, for example, [9, 10]), which were present in the sample as a result of its additional doping with aluminium ions.

When a ZnSe: Fe<sup>2+</sup> sample is excited by electron impact, the beam electrons in the sample should affect the luminescence kinetics of Fe<sup>2+</sup> ions. Let us consider the electron-impact excitation of luminescence in a ZnSe: Fe<sup>2+</sup> sample. The sample is located on the anode of the electron gun. Electrons accelerated in a vacuum are incident on a sample and, having lost energy in a thin surface layer of the material due to the excitation of electron–hole pairs and the material heating, they populate the conduction band and drift in the sample under the influence of an electric field produced by an external source. For an accelerating voltage of 40 kV, the mean free path of electrons in ZnSe can be estimated as 4–5  $\mu$ m (see, for example, [11]), with the sample thickness being much larger than the indicated value. We believe that excited Fe<sup>2+</sup> ions are formed in this region, the luminescence of which was measured. When current flows in the sample, there arises a volume charge consisting of conduction electrons. After removing the voltage from the anode, this charge flows to a grounded anode. We assume that the resistance of the sample–anode transition is zero, and that the excitons formed in the sample under the action of electron impact after the voltage is removed from the anode are illuminated for a time much shorter than the electron pulse duration. The basis for this is the data of [12], where the exciton emission time in ZnSe was measured at a temperature of 18 K, which turned out to be  $\sim 0.2$  ns. Therefore, in further calculations concerning the description of the luminescence kinetics after the end of the electron pulse action, we assume that excitons are absent. Part of free electrons can be trapped in the band gap, but we do not take this into account in the calculations.

Free electrons in the sample interact with the excited Fe<sup>2+</sup> ion and quench its luminescence due to the Auger effect. Let us describe the process of the luminescence decay of an impurity taking this effect into account. The equation for the time dependence of the concentration  $n_c$  of excited Fe<sup>2+</sup> ions after the voltage is removed from the anode and the current pulse ceases to flow has the form

$$\frac{dn_c}{dt} = -\beta n_c n_c - \frac{n_c}{\tau_r}. \quad (1)$$

Here,  $n_c$  is the concentration of free electrons in the sample;  $n_c/\tau_r$  is the rate of a change in the concentration of excited Fe<sup>2+</sup> ions, due to the finite value of  $\tau_r$ ;  $\beta$  is the constant of interaction of excited ions and free electrons; and the term  $-\beta n_c n_c$  describes the rate of a decrease in the concentration of excited Fe<sup>2+</sup> ions due to the Auger effect. The possible presence of Fe<sup>3+</sup> ions, which should be formed by an electron impact, as well as the recombination of Fe<sup>3+</sup> and electrons, are not considered in this work, since we assume that the Fe<sup>3+</sup> + e<sup>-</sup>  $\rightarrow$  Fe<sup>2+</sup> reaction occurs rather quickly. We note here that in the sample there may be also present free electrons bonded, for example, with dopants. The concentration of such electrons does not depend on time; therefore, their presence will lead to a decrease in the time  $\tau_r$  due to quenching by the free electrons of the excited state of Fe<sup>2+</sup>.

Equation (1) should be supplemented by an equation describing the dependence of the electron concentration on time. Let us find this dependence. The total current of accelerated electrons is constant in each section of the electron beam both in vacuum and in the crystal. Let the current be constant during the electron pulse action (rectangular current pulse) and equal to  $I_0$ . The drift velocity of free electrons in the sam-

ple is  $v = \mu E_{\text{in}}$ , where  $E_{\text{in}}$  is the electric field strength in it, due to the voltage applied to the anode, and  $\mu$  is the electron drift mobility. The total electron current in the sample is expressed as

$$I_0 = Sq n_e \mu E_{\text{in}}, \quad (2)$$

where  $S$  is the cross-sectional area of the electron beam in the sample, and  $q$  is the electron charge.

Let us find the field  $E_{\text{in}}$  in the sample during the action of the electron current pulse. To simplify the calculations, we assume that the anode is a conducting ball of radius  $R$ , on the surface of which there is a thin sample. We also assume that the sample covers the entire surface area of the ball. At the anode potential  $U_a$ , a charge  $Q_a = C_a U_a$  will reside on it. The field inside the sample is  $E_{\text{in}} = Q_a / (4\pi\epsilon_0\epsilon R^2)$ , where  $\epsilon_0$  is the permittivity of the vacuum and  $\epsilon$  is the permittivity of the sample. We assume that the anode capacity is  $C_a = 4\pi\epsilon_0 R$  [13]. We also assume that the sample thickness  $h$  is small ( $h \ll R$ ), and we neglect its contribution to the anode capacitance. Then,

$$E_{\text{in}} = \frac{U_a}{R\epsilon}. \quad (3)$$

From (2) and (3) we obtain the expression for the concentration of free electrons in the sample (in the volume charge region) during the passage of a current pulse through it:

$$n_e = \frac{I_0 R \epsilon}{Sq \mu U_a}. \quad (4)$$

We assume that the electron beam current density is constant in the sample cross section; then, in the model under consideration, the electron concentration of this current is uniform within the charged region of the sample. After removing the voltage from the anode and the termination of the current pulse action, the excess charge passes through the surface of the sample, which is in contact with the anode, to the ground.

We find the equation for changing the concentration of free electrons in the sample after removing the voltage from the anode. The continuity equation for the electron concentration can be written as

$$\frac{\partial n_e}{\partial t} + \text{div}(n_e \mu \mathbf{E}) = 0.$$

For the electric field  $\mathbf{E}$ , we have the equation

$$\text{div}(\epsilon_0 \epsilon \mathbf{E}) = q n_e.$$

It follows from these equations that

$$\frac{\partial n_e}{\partial t} + \mu \frac{q n_e^2}{\epsilon \epsilon_0} + (\mathbf{E}, \nabla n_e) \mu = 0.$$

Here, the electric field  $\mathbf{E}$  is the volume charge field, which should be determined by taking into account the boundary conditions in the specific geometry of the problem. We can find a solution to the last equation for a flat sample, when the initial distribution of the electron concentration is independent of the coordinate. In this case, the electron concentration at each moment of time does not depend on the coordinates

within the charged region, and its dependence on time is determined by the equation

$$\frac{\partial n_e}{\partial t} + \mu \frac{q n_e^2}{\epsilon \epsilon_0} = 0. \quad (5)$$

In our case, we can assume that the initial concentration of free electrons in the sample is constant, including in the region where  $\text{Fe}^{2+}$  ions are electron-impact excited. Equation (5) has a solution

$$n_e(t) = n_e(0) \left[ 1 + \mu \frac{q}{\epsilon \epsilon_0} n_e(0) t \right]^{-1}, \quad (6)$$

where  $n_e(0)$  is the concentration of free electrons at the time of removal of voltage from the anode.

Substituting (6) into (1) and solving the resulting equation, we find the expression

$$\ln \left[ \frac{n_e(t)}{n_e(0)} \right] = -a \ln \left( 1 + \frac{t}{\tau_e} \right) - \frac{t}{\tau_r} \quad (7)$$

for the time dependence of the concentration of excited ions. Here,  $n_e(t)$  is the concentration of excited centres as a function of time (time  $t = 0$  corresponds to the removal of voltage from the anode);  $a = \beta \epsilon \epsilon_0 / (\mu q)$ ; and

$$\tau_e = \frac{\epsilon \epsilon_0}{q \mu n_e(0)} \quad (8)$$

is the characteristic relaxation time of the charge. Substituting expression (4) into (8) and assuming that  $n_e = n_e(0)$ , we obtain

$$\tau_e = \frac{S_a C_a U_a}{S_a I_0}, \quad (9)$$

where  $S_a = 4\pi R^2$  is the surface area of the anode. Note that expression (9) contains the quantity  $\tau = C_a U_a / I_0$ , which is the time that is characteristic of the experimental setup.

Equation (7) describes the time dependence of the luminescence intensity of excited centres, because it is proportional to the concentration of these centres. Figure 1 shows the dependence calculated by formula (7) (curve 3), which was plotted with parameters  $\tau_e = 0.47 \mu\text{s}$ ,  $\tau_r = 65 \mu\text{s}$ , and  $a = 0.13$ , which provide the best agreement with experimental data. It can be seen that the dependence describes the experimental data well both at short times, immediately after the end of the electron pulse action, and at times exceeding  $50 \mu\text{s}$ .

The electron concentration calculated using equation (8) at the moment of voltage removal from the anode is  $n_e(0) = 3.6 \times 10^{10} \text{ cm}^{-3}$  ( $\mu = 0.026 \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$  [11],  $\epsilon = 8.1$  [14]). Note that even such a low concentration of free electrons affects the lifetime of the excited state of the  $\text{Fe}^{2+}$  ion.

From the experimentally found value  $a = 0.13$ , we can estimate the constant  $\beta$ . If we assume the electron drift mobility  $\mu$  in the ZnSe crystal to be equal  $0.026 \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$  [11], then we obtain the constant of interaction of free electrons with the excited  $\text{Fe}^{2+}$  ion,  $\beta = 7.6 \times 10^{-12} \text{ m}^3 \text{ s}^{-1}$ . The values of the electron concentration and the constant  $\beta$  are estimates, because for this sample the value of the mobility of free electrons is unknown.

The problem of the efficiency of the quenching of excited state of the  $\text{Fe}^{2+}$  ion by the secondary electrons and holes that arise during the deceleration of an electron in a medium

requires a separate consideration. The fundamental possibility of obtaining radiation amplification by using Fe<sup>2+</sup> impurity ions and exciting them by electron impact depends on the solution to this problem.

#### 4. Conclusions

1. The kinetics of the luminescence decay of Fe<sup>2+</sup> ions in ZnSe is measured upon its excitation by a short pulse of accelerated electrons at nitrogen temperature. The obtained time dependence of the luminescence intensity noticeably differs from the exponential one, which is observed upon excitation of luminescence by a short light pulse.

2. The observed time dependence of the luminescence intensity of Fe<sup>2+</sup> ions in ZnSe is explained. The theoretical description is based on the Auger effect of the quenching of luminescence of an Fe<sup>2+</sup> impurity in a crystal by free electrons of the volume charge of the electron beam current. It is shown that the relaxation of the volume charge substantially affects the decay kinetics of the luminescence of Fe<sup>2+</sup> ions, which is observed after the accelerated electron pulse terminates its action on the ZnSe:Fe<sup>2+</sup> sample.

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