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Free-electron Auger quenching of the Fe^{2+} excited state in ZnSe

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Abstract. **The influence of free electrons in Fe^{2+}:ZnSe crystals on the nonlinear transmission of high-power laser radiation with a wavelength of 2940 nm at room and low temperatures is experimentally found. Fe^{2+}:ZnSe samples additionally doped with Al are used. The transmission of an Al:Fe:ZnSe sample with electron conduction in a strong (peak intensity about 4.6 MW cm^{-2}) field is almost the same as in a weak field both at low and room temperatures. The absence of an increase in the transmission of this sample under the action of high-power radiation is explained by increasing absorption saturation intensity of Fe^{2+} at this wavelength due a decrease in the lifetime of the excited state of Fe^{2+}. The decrease in the lifetime is related to the well-known Auger quenching of impurity luminescence in semiconductors by free electrons.**

Keywords: *auger effect, free electrons, Fe^{2+}:ZnSe, nonlinear transmission.*

1. Introduction

One of materials used for the development of solid-state lasers operating in the wavelength region near 4 μm is a ZnSe crystal doped with Fe^{2+}. Lasing in this crystal was reported for the first time in [1]. A specific feature of this material is a strong temperature dependence of the lifetime of the upper iron level [1], which changes from 105 μs at 120 K [1] to 335 ns at 300 K [2]. This feature is explained in the literature by intersection of the configuration potential curves of electronic states of Fe^{2+} in ZnSe and by a strong electron–phonon coupling (see, e.g., [3]).

However, it is well known that the luminescence of impurity centres in semiconductors is quenched due to the excitation energy transfer to free charge carriers or shallow impurity centres, which causes their ionisation (Auger effect). There is a rather large number of works devoted to this effect. Not pretending to completeness, we will mention several works which, in our opinion, are most close to the subject of our study. In particular, in [4] it was shown that free carriers in Mn:ZnSe affect the Mn^{2+} luminescence kinetics by decreasing the lifetime of the upper level of the impurity. The authors of [5] studied Auger quenching of Mn^{2+} ions in electrically conductive (Mn, Y):CdF_2 crystals. It was shown that the presence of free electrons leads to a decrease in the lifetime of the excited state of Mn^{2+} due to the Auger effect. It was also observed in this work that, in (Mn, Y):CdF_2 crystals with low Y concentrations, the energy transfer from excited Mn^{2+} ions to free electrons is by 500 times more probable than to shallow impurity centres. The electroluminescence of Er in Si crystals was studied in [6, 7], and it was shown that Auger quenching of luminescence by free carriers leads to a considerable decrease in the quantum efficiency of electroluminescence in devices based on indirect-gap semiconductors.

The rate of the Auger decay of excited states of impurity centres is directly proportional to the concentration of free carriers. It was experimentally observed in aforementioned works [4–7] that the luminescence decay time decreases with increasing temperature due to an increase in the free-carrier concentration.

We can suggest that the temperature dependence of the luminescence decay time of Fe^{2+} ions in ZnSe crystals is also explained by the Auger quenching of luminescence by free electrons. With increasing temperature, free electrons in the conduction band may appear due to depletion of traps with energy levels in the crystal band gap. The existence of these levels can be related to lattice defects or uncontrolled impurities in ZnSe.

The aim of the present work is to qualitatively verify the influence of free carriers in Fe^{2+}:ZnSe crystals on the lifetime of the excited state of the Fe^{2+} ion. Since the luminescence quantum yield of the Fe^{2+} ion at room temperature is low (~0.001), the luminescence decay time is difficult to measure. Therefore, we studied the nonlinear transmission of Fe^{2+}:ZnSe crystals. This method allows one to measure the absorption saturation intensity at a probe wavelength. This intensity is inversely proportional to the luminescence decay time and, hence can be used to estimate this time. This method works especially well in the case of strongly quenched impurity centres. Free carriers in Fe^{2+}:ZnSe samples were created by additional doping with Al.

2. Experimental

The setup used for measuring the nonlinear transmission of samples, as well as the procedure of measuring and data processing, is described in [8, 9]. Here, we only mention that transmission was measured by two PD29 photodetectors, which recorded signals at the input and output of the sample. The transmission measurement error is estimated to be 2%. The peak (in the transverse distribution maximum) input energy density at a wavelength of 2940 nm was 1.2–1.3 J cm^{-2}, the pulse duration was 280 ns, and the peak intensity was 4.6 MW cm^{-2}. The input laser beam cross section area was 0.0052 cm^2. After processing the measurement results, we

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determined the time dependence of the sample transmission coefficient during the action of a high-power laser pulse.

We measured transmission for high-power and 200-fold attenuated radiation. Below, all transmittances measured at a high power (in a strong field) are denoted by s. The transmittances measured under attenuated irradiation (in a weak field) are denoted by w.

The method for fabrication of zinc selenide samples codoped with iron and aluminium ions consisted in the following. First, CVD-ZnSe samples were doped with iron ions. An iron film ~1 μm thick was deposited on the polished surface of a sample by electron-beam sputtering, after which the sample was placed into a gasostat chamber and diffusion doped under conditions of hot isostatic pressing at a temperature of 1250°C and argon pressure in the chamber P = 950 MPa. The sample treatment time was 22 h. Then, the sample was placed into a quartz ampoule with an aluminium source in a graphite crucible and diffusion annealed in a Zn atmosphere for 20 h at 1050°C. Prior to optical measurements, we performed high-quality chemical-mechanical polishing of the obtained sample. A parallelepiped 5 × 5 × 3 mm in size was cut out of the doped sample for measuring the Hall effect. It was found that the obtained sample had n-type conduction at a free-electron concentration of 7×10^{15} cm^{-3}. Below, we will denote this sample by No. 704.

The transmission spectrum of sample No. 704 at room temperature in the wavelength range 1500–25000 nm is shown in Fig. 1a. One can see a decrease in the sample transmission at wavelengths exceeding 5000 nm, which is caused by absorption by free electrons. To determine the portions of 2940-nm radiation absorbed by Fe^{2+} ions and by free electrons, we plotted the wavelength dependences of the optical density of samples (Fig. 1b).

The optical density related to the absorption by free carriers is described by the phenomenological power function $D_f(\lambda) = a(\lambda/\lambda_0)^m$, where λ_0 = 10000 nm, a = 10.8, and m = 3.15 (wavelengths λ are expressed in nanometers). This function best describes the experimental data. As a result, we found that the sample transmission at a wavelength of 2940 nm with allowance for reflection from faces is T_{exp} = 30%, the transmission of centres is T_c = 38%, and the transmission in the case of absorption by free electrons is T_{free} = 80% (the latter value is the maximum possible transmission of the sample in a strong field). Figure 1b presents the optical density of the sample, the optical density related to the absorption by free electrons, and the optical density due to the absorption by Fe^{2+} ions.

Figure 2 shows the time dependences of the sample transmission during the pulse action. One can see that the sample transmission at room temperature changes during the high-power pulse action by about 2%, which is close to the measurement error. At a low temperature, the transmission changes within the range 2%–3%, while the maximum transmission of the sample is 26%–28%. This value is considerably lower than the maximum possible transmission (80%) estimated above from the transmission spectra at room temperature (see Fig. 1). It is necessary to note that the transmittances measured in different regions of the sample somewhat differ from each other, which is obviously related to the sample inhomogeneity.

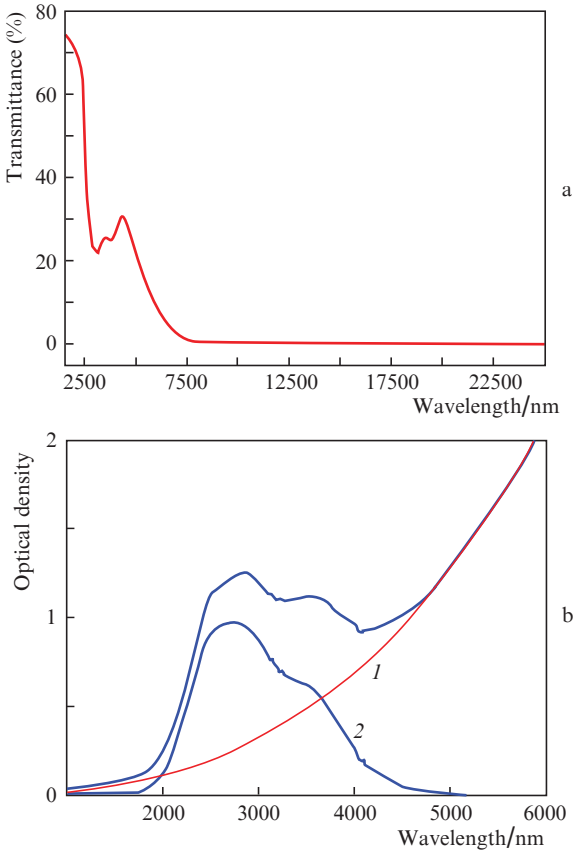

Figure 1. (a) Transmission spectrum of Al-doped Fe^{2+}:ZnSe sample No. 704 and (b) optical density ln(1/T) of this sample, as well as of (*1*) free carriers and (*2*) impurity centres in the sample. T is transmittance.

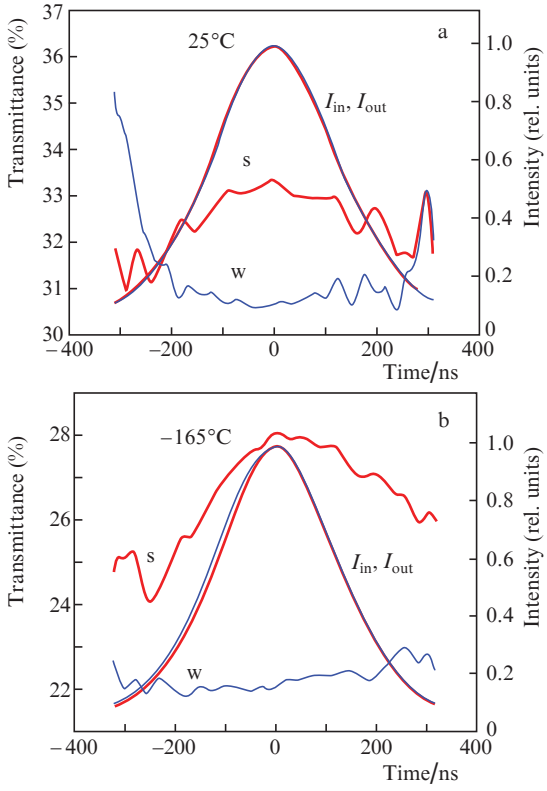

Figure 2. Time dependences of the sample transmission and the input (I_{in}) and output (I_{out}) laser pulse intensities under conditions of strong (s) and weak (w) fields at different temperatures.

3. Discussion of measurement results

The absence of changes in the transmission of the Al-doped sample in a strong field is explained by the fact that the intensity of radiation used in our experiment was insufficiently high to cause noticeable changes in the sample transmission.

Let us estimate the absorption saturation intensity in the sample based on the obtained experimental data. The propagation of a plane wave in a medium with saturation is described by the well-known equation (see, e.g., [10, 11]) $dI/dz = -\alpha_0 I(1 + I/I_s)^{-1}$, where I is the radiation intensity in the medium, I_s is the absorption saturation intensity, and α_0 is the unsaturated absorption coefficient. From this equation, we can estimate the saturation intensity by the formula $I_s \approx I_{in}(T_0/\Delta T)(1-T_0)$, where T_0 is the sample transmission in a weak field, ΔT is the change in transmission under action of high-power radiation ($\Delta T \ll T_0$), and I_{in} is the radiation intensity at the entrance to the sample. Then, at I_{in} = 4.6 MW cm^2, $T_0 = 0.33$, and $\Delta T < 0.02$, we find the saturation intensity $I_s > 50$ MW cm^{-2}. From this intensity value, we can estimate the upper bound of the excited state lifetime. The absorption saturation intensity when the upper level of the resonance transition rapidly relaxes to an intermediate level is $I_s = \hbar\omega/\sigma\tau$, where $\hbar\omega$ is the photon energy, σ is the absorption cross section, and τ is the lifetime of the excited state of the centre. At the Fe^{2+} absorption cross section in ZnSe at a wavelength of 2940 nm $\sigma = 10^{-18}$ cm^2 [1] and the photon energy $\hbar\omega = 0.68 \times 10^{-19}$ J, we estimate the lifetime τ of the upper Fe^{2+} level to be shorter than 1.3 ns.

The lifetime in ZnSe samples doped only with Fe^{2+} at room temperature is 355 ns [2], and the saturation intensity is $I_s = 0.2$ MW cm^{-2}. The increase in the absorption saturation intensity for the resonance radiation in the Fe : Al : ZnSe sample is explained by a decrease in the lifetime of the Fe^{2+} excited state, which we explain by the well-known effect of Auger quenching by free electrons (see, e.g., [4, 5]).

The slight increase in the transmission at a low temperature that is seen in Fig. 2b can be explained by a decrease in the density of free electrons (Al ionization energy in ZnSe is about 26.3 meV [12]) with decreasing temperature. However, the shape of the time dependence of transmission in Fig. 2b does not follow the laser pulse shape, as it should be if the excited state lifetime is considerably lower than the probe pulse duration. This obviously occurs due to the sample inhomogeneity, i.e., to the existence of regions with weakly quenched Fe^{2+}.

The obtained results allow us to conclude that the majority of Fe^{2+} ions in the sample at room temperature are completely quenched, which is caused by the relatively high concentration of Al, which is a shallow donor. The excited Fe^{2+} ion interacts both with free electrons of the conduction band and with the Al impurity centre, when its ionisation occurs via the Auger excitation energy transfer. It is shown in [5] that excited impurity in (Mn, Y) : CdF_2 interacts with free electrons much more efficiently than with shallow donors because the energy of interaction with the latter strongly decreases with increasing distance between the impurity and the shallow donor. Therefore, we suggest that the main contribution to quenching of Fe^{2+} ions is made by free electrons.

4. Conclusions

1. The Fe^{2+} : ZnSe sample doped with Al is almost not bleached at room and low temperatures under action of high-power laser radiation. We suggest that this occurs due the interaction of Fe^{2+} with free electrons, which leads to shortening of the Fe^{2+} excited state lifetime due to the Auger effect and to an increase in the intensity of the resonance radiation absorption saturation.

2. It is necessary to perform additional experiments to study the degree of the effect of free carriers on the lifetime of the Fe^{2+} excited state in ZnSe crystals. Improvement of the growth technology of Fe^{2+} : ZnSe crystals can probably increase the lifetime of the Fe^{2+} excited state at room temperature and create samples with a room-temperature lifetime as long as at low temperatures.

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