

Proceedings of the XX International School of Semiconducting Compounds, Jaszowiec 1991

## RECOMBINATION PROCESSES IN ZnSe:Eu

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The photo-ESR and photoluminescence experiments have been performed on high-resistivity ZnSe:Eu crystals. We report the first evidence that the energy level of  $\text{Eu}^{2+}$  ground state is located within the ZnSe forbidden gap, approximately 2.1 eV below the bottom of the conduction band.

PACS numbers: 71.55.Gs, 76.30.Kg, 78.50.Ge

Contrary to practically all transition-metal impurities only some rare-earth (RE) ions have been assumed to introduce energy levels into the forbidden gap of II-VI compounds [1]. Recently, we have analyzed this problem in ZnS and other sulphides doped with RE ions [2]. Until now, the only RE impurity observed in ZnSe lattice in 2+ charge state is europium [3]. In this communication we present the first evidence that the  $\text{Eu}^{2+}/^{3+}$  energy level is located within the ZnSe gap.

The electron spin resonance (ESR) experiments were performed on a Bruker 418s X-band equipped with an Oxford Instruments ESR-900 continuous-gas-flow cryostat, working in the temperature range of 4–300 K. A high-pressure XBO 150 xenon lamp and a set of Carl-Zeiss interference filters were used for the optical excitation. The photo-ESR experiments have been performed on high-resistivity ZnSe:Eu crystals. An ESR signal of  $\text{Eu}^{2+}(4f^7)$  has been observed at 4.2 K prior to illumination. After illuminating the sample with  $h\nu_1 > 1.9$  eV light a quenching of the intensity of this signal has been observed, i.e., the concentration of  $\text{Eu}^{2+}$  centers was found to decrease due to the population of the  $\text{Eu}^{3+}(4f^6)$  state which cannot be easily detected by ESR technique. Then the light was turned off and a small increase of the  $\text{Eu}^{2+}$  ESR signal was observed. After equilibrium was reached, a secondary infrared illumination ( $0.9 \text{ eV} < h\nu_2 < 1.1 \text{ eV}$ ) was applied leading to rapid enhancement of the  $\text{Eu}^{2+}$  signal intensity. Still a small, further increase occurred after the light was turned off. The sequence of steps in the experiment is shown in Fig. 1. Before each measurement, a primary  $h\nu_2$  illumination was applied to ensure the same initial conditions. The spectral distribution of the photoquenching rate constant ( $\tau^{-1}$ ) normalized to constant light intensity is shown in Fig. 2.

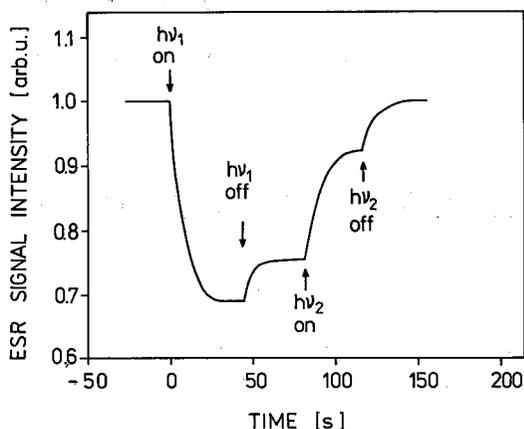


Fig. 1. The sequence of steps in the photo-ESR experiment. Kinetics of the intensity of the  $\text{Eu}^{2+}$  ESR signal under the primary  $h\nu_1 = 2.2$  eV and secondary  $h\nu_2 = 1$  eV illumination are shown.

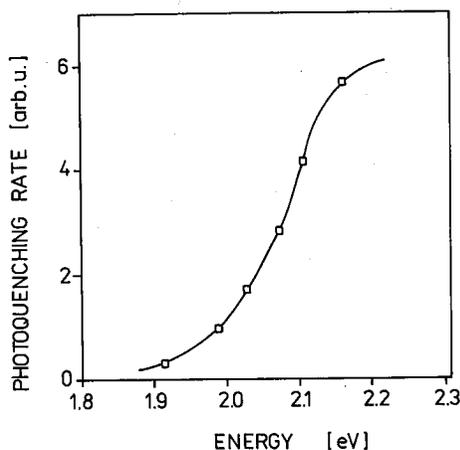


Fig. 2. The spectral dependence of the  $\text{Eu}^{2+}$  photoquenching rate measured at 4.2 K. The solid curve represents the fit to the experimental data with formulas (1) and (2).

We attribute the first transition ( $h\nu_1 > 1.9$  eV) to the direct  $\text{Eu}^{2+} + h\nu_1 \Rightarrow \text{Eu}^{3+} + e_{\text{CB}}$  photoionization. By solving the appropriate kinetic equations [4] it can be shown that  $\tau^{-1}(h\nu)$  is proportional to the optical cross-section  $\sigma(h\nu)$  for this transition. Thus, the spectral dependence of the  $\text{Eu}^{2+}$  ionization can be determined. Since for the description of a smooth band observed in a narrow energy range an elaborate theoretical approach is not justified, we used the simple

Kopylov-Pikhtin formula [5]:

$$\sigma(E_{\text{opt}}, h\nu) \propto (h\nu - E_{\text{opt}})^{1/2} (h\nu)^{-3}. \quad (1)$$

Because in a partly ionic compound the change of a center's charge state is accompanied by a relaxation of the lattice around the ionized ion, this formula was extended to account for the electron-phonon interaction in the manner proposed by Langer et al. [6]:

$$\sigma(h\nu) = \pi^{-1/2} \int_{-\beta}^{\infty} dz \sigma_{\text{el}}(E_{\text{opt}}, h\nu + \Gamma z) (1 + \Gamma z/h\nu) \exp(-z^2), \quad (2a)$$

$$\beta = (h\nu - E_{\text{opt}})/\Gamma \quad (2b)$$

$$\Gamma = \frac{\omega_0}{\omega_{\text{ex}}} \left[ 2(E_{\text{opt}} - E_{\text{th}}) \hbar\omega_0 \operatorname{cth} \left( \frac{\hbar\omega_0}{2kT} \right) \right]^{-1/2}. \quad (2c)$$

From the fit we have obtained the thermal and optical ionization energies of  $\text{Eu}^{2+}$  impurity:  $E_{\text{th}} = 1.9 \pm 0.1$  eV and  $E_{\text{opt}} = 2.1 \pm 0.1$  eV, respectively.

The complementary photoneutralization transition  $\text{Eu}^{3+} + h\nu_2 \Rightarrow \text{Eu}^{2+} + h\nu_{\text{VB}}$  has been observed for  $0.7 \text{ eV} \leq h\nu_2 \leq 1.1 \text{ eV}$  as an increase of the  $\text{Eu}^{2+}$  ESR signal intensity. This part of measurements is less accurate due to competition of many extra processes leading to both stimulation and quenching of  $\text{Eu}^{2+}$ , i.e., the capture of electrons ionized from donors into the conduction band, capture of holes generated in the valence band in the ionization process of chromium and copper-related defects (Cr and Cu are contaminants in our samples).

The photosensitivity of the  $\text{Eu}^{2+}$  charge state must mean that  $\text{Eu}^{3+}$  is present, or can be obtained in the ZnSe host. The proper excitation mechanism of the  $\text{Eu}^{3+}$  luminescence is still a separate problem recently discussed by us for ZnS:Eu [9]. The efficient charge transfer between  $\text{Eu}^{2+}$  and  $\text{Cr}^{3+}$  indicates that europium can act as a recombination center of free carriers generated in conduction and valence band of ZnSe. In the photoluminescence experiments we observed well known emission bands associated with the presence of Cu impurity, namely the green (2.34 eV), red (1.95 eV) and infrared (1.41 eV) emissions [7, 8]. In these studies we have not observed any  $\text{Eu}^{3+}$ -related intra-ion emission.

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