$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ IONIZATION TRANSITION IN ZnSe*

M. SURMA, M. GODLEWSKI
Institute of Physics, Polish Academy of Sciences
Al. Lotników 32/46, 02-668 Warszawa, Poland
AND T.P. SURKOVA
Institute of Metal Physics, Russian Academy of Sciences
Kovalevskaya 18, 620219 Ekaterinburg, GSP-170, Russia

Detailed photo-ESR study of iron and chromium impurities in ZnSe is presented. The energy level position of Fe $2+ / 3+$ energy level is determined. The role of iron and chromium impurities in nonradiative recombination processes is discussed.
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1. Introduction

ZnSe is one of the most promising II–VI compounds for opto-electronics. It can be used for construction of blue laser diode [1]. The latter stimulated current interest in the optical properties of this material. This includes the studies of centers of nonradiative recombination in ZnSe.

Iron is the most common inadvertent dopant in ZnSe [2] and likely an efficient center of the nonradiative recombination. Such role of the iron impurity was clearly evidenced by our previous studies of ZnS [3, 4]. In this communication we present the results of photoluminescence, photo-ESR and optical absorption investigations of Fe doped ZnSe. The aim of these studies was to elucidate the role of Fe ion in the radiative recombination processes in ZnSe.

2. Iron ionization transitions

Even though iron is an inadvertent dopant in ZnSe, its role in the optical and electrical properties of ZnSe was not understood. There was large scatter of the data on the energy level position of iron $2+ / 3+$ energy level in ZnSe band gap. The values from about 0.75 eV [5], 1.1 eV [6], less than 1.3 eV [7] above the valence band (VB) edge to 0.81 eV below the conduction band (CB) edge [8] were given. Most of those data was derived from the photo-ESR experiment. In Fig. 1a,b we

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M. Surma, M. Godlewski, T. P. Surkova present the set of the spectral dependencies of photoexcitation and photoquenching of Fe$^{3+}$ and Cr$^+$ ESR signals measured in either intentionally chromium or iron doped sample. In any case iron, chromium, manganese and copper were identified from ESR and photoluminescence (PL) experiments either as intentional dopants or contaminants. The data shown in Fig. 1 explain the source of the large scatter of the iron ionization energies. All the spectra recorded have complex nature and their interpretation must be based on several complementary investigations.

Our interpretation is based on detailed knowledge of chromium ionization transition in ZnSe [9]. The Cr$^+$ excitation spectrum (a1) consists of two bands (II and III) attributed to direct chromium ionization (II) and indirect process (III) of Cu acceptor ionization accompanied by capture of some of the photoexcited electrons by Cr$^{2+}$ centers. Band III dominates even for the sample heavily doped with Cr. This proves large electron capture rate by Cr$^{2+}$ ion. A slightly different excitation spectrum is observed for intentionally iron doped sample (a2). Here band III is weaker than previously and a new band (I) is observed. This band is stronger in Fe$^{3+}$ excitation spectrum which is dominated by band II of direct chromium ionization. Band III is missing. It is paradoxical to notice that the best condition to measure direct chromium ionization is to measure indirect excitation process of iron Fe$^{3+}$ ESR signal. Comparing the data depicted in Fig. 1a we attribute band I

![Fig. 1](image-url). Spectral dependence in arbitrary units of photoexcitation (a) and photoquenching (b) of Cr$^+$ (a1, a2, b2) and Fe$^{3+}$ (a3, b1) ESR signals in ZnSe:Cr (a1) and ZnSe:Fe (a2, a3, b1, b2). Different spectral regions are marked with I–VII and their interpretation is given in the text.
to direct $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ photoionization. This localizes $2^+ / 3^+$ energy level of iron at 1.1 eV above VB edge. Optical cross-section for $2^+$ to $3^+$ Fe ionization was too small for accurate optical absorption measurements [10].

The above interpretation is verified by the experimental data shown in Fig. 1b. $\text{Fe}^{3+}$ photoquenching is observed for above 1.1 eV illumination, due to the complementary VB–iron ionization transition. For higher energies $\text{Fe}^{3+}$ ESR signal is photostimulated, as for (a3) spectrum. Then, the photo-quenching of $\text{Cr}^+$ ESR signal occurs due to hole trapping by chromium. The same mechanism explains the origin of band V. Holes induced in the VB band in photoneutralization transition of Cu acceptor are trapped by $\text{Cr}^+$ centers. For higher energies direct photoneutralization of chromium occurs (VI) followed by threshold for band–band transitions.

![Figure 2](image)

Fig. 2. Photoluminescence spectrum of iron doped ZnSe (inset). Visible PL consists of red Cu-related donor–acceptor pair (DAP) emission. In infrared strong about 1 µm emission was observed due to $^3T_1 \rightarrow {}^5E$ emission of $\text{Fe}^{2+}$. The relative ratio of the intensities of this emission to the total emission is depicted. Large experimental error is related to uncertainty of iron concentration in the sample.
3. Nonradiative recombination processes

The photo-ESR data allow us to conclude on the role of iron and chromium in nonradiative recombination processes in ZnSe. The spectrum (a3) shows that even though direct ionization is not efficient, iron is efficient electron and hole trap in ZnSe. Holes induced in VB in Cr ionization are readily captured by Fe$^{2+}$ (strong band II in (a3)). This also occurs for electron trapping by Fe$^{3+}$. However, these processes must be more efficient for Cr ion. Band III still dominates in spectrum (a2) even though the sample was heavily doped with Fe, i.e., electrons are still trapped by neutral Cr$^{2+}$ ions. This process successfully competes with electron trapping by positively charged Fe$^{3+}$. Also hole trapping (band V) is still efficient for Cr ion in intentionally iron doped sample. Our conclusion on moderate efficiency of iron related nonradiative recombination is confirmed by the data shown in Fig. 2. A noticeable deactivation of the Cu red PL occurs for iron concentration larger than $5 \times 10^{17}$ cm$^{-3}$.

References