

Magnetic and luminescent properties of vanadium-doped ZnSe crystals



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ABSTRACT

Magnetic and photoluminescence properties of vanadium-doped ZnSe crystals with impurity concentrations varied by changing the V amount in the source material from 0.03 to 0.30 at% are studied in 5–300 K temperature range. Investigation of magnetic properties shows that the studied concentrations of vanadium impurity that should not disturb crystal lattice are insignificant for observing ferromagnetic behaviour even at low temperatures. The contribution of V impurity to edge emission and its influence on infra-red emission are discussed. Similarities of magnetic and luminescent properties induced by vanadium and other transition metal impurities are discussed.

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1. Introduction

Transition metal (TM) impurities in semiconductors have attracted great attention in recent years because of their interesting properties, both in technological and fundamental points of view [1,2]. One of the most important practical applications of these impurities is elaboration of the tunable lasers for the infra-red (IR) spectral range on the basis of TM doped wide band-gap materials [3]. Particularly, zinc selenide crystals doped with transition metal ions (e.g. V, Cr, Fe, Co, Ni) can be used in fabrication of active media and passive Q switches for the telecommunication technologies, wave optics, biology, and medicine [4]. One of the most surprising features of TM impurities in semiconductors, which makes these materials interesting also for the fundamental research, is that they can possess several charge states separated by a fraction of the host energy gap in contrast to the much larger difference in the atomic ionization potentials [5]. This interest led to intensive theoretical study of the positioning of the TM ion levels within the semiconductor materials bandgap [5,6]. Thus, experimental research in this direction was not only limited to investigation of the materials properties perspective for the practical applications, but also included fundamental study of the charge transfer processes,

allowing to confirm theoretically established positions of the impurity levels within the semiconductor bandgap.

For some elements from the TM group, this problem is almost completely solved, for other, like, for example vanadium, theoretical and experimental results presented by various research groups are contradictory [7] and agreement between the theory and experiment in some cases is fairly poor [8]. Study of optical absorption [9], emission [8] and excitation spectra [10] of the vanadium-doped II–VI compounds allowed to determine the thresholds energies for the charge transfer processes involving V ions. However, exact association of these energies with the vanadium impurity levels is disputable until now [10].

At the same time, materials based on II–VI semiconductor compounds, in which a fraction of the nonmagnetic cations (e.g. Zn²⁺) has been randomly replaced by TM ions, are widely known as diluted magnetic semiconductors (DMS) [11]. DMS are actively studied with the aim to use both charge and spin of electrons in semiconductors. Spin injection into non-magnetic semiconductors is needed due to the potential to create a new class of spintronic devices, which could be easily incorporated in the conventional electronic circuits [12]. However, direct injection of spin-polarized electrons using a ferromagnetic metal for a metal-semiconductor junction is inefficient because of scattering of the spin-polarized carriers at the Schottky barrier [12,13]. In order to overcome this problem, DMS with ferromagnetic properties at room temperature may be used. It was theoretically predicted that vanadium-doped and chromium-doped ZnSe should induce ferromagnetism above

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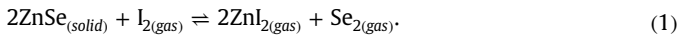
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room temperature without additional carrier doping [14,15]. However, despite this fact, the number of papers on magnetic properties of vanadium-doped II–VI compounds is very limited [16,17]. It was shown that the crystallinity of the samples become worse by vanadium doping and at concentrations ~ 4 at% V ferromagnetism could not be found because the vanadium atoms in ZnSe crystal were substituted for the Se-site and/or existed in interstitial sites [18].

Historically, the magnetism of doped wide bandgap semiconductors and their optical properties have been considered separately in relation to different tasks. However, DMS, which combine both magnetic and optical properties, seem to be the most novel and interesting objects for investigation not only because of their fundamental properties (e.g. giant Faraday rotation or giant exciton splitting) [19], but also because of their practical applications in magneto-optics, magneto-electronics [20,21] and, as mentioned above, spintronics. In this paper, we continue [22–25] the complex investigation of the TM doping effect on magnetic and luminescent properties of the zinc selenide crystals. The influence of the V impurity concentration on the magnetization and photoluminescence (PL) of ZnSe, as well as correlation between these properties, are analyzed. Comparison between vanadium and other TM dopants is made.

2. Sample preparation and experimental techniques

Vanadium-doped ZnSe samples with V concentrations varied within 0.00–0.30 at% range were grown by the chemical vapor transport (CVT) method using iodine as a transport agent. The doping was performed during the growth process. The growth technique is based on interaction of a gaseous agent A with a non-volatile substance X (material for the crystal growth). Depending on external conditions (temperature and partial pressures) formation of various gaseous molecules of the A_pX_d type takes place. Change of these external conditions may lead to decomposition of the volatile compound with separation of the substance X . Thus, for the crystallization of X , it is necessary to create a temperature gradient and to place in it the source material X and the transportation agent. In this case, at some temperature T_1 in the source zone, formation of the volatile molecules A_pX_d will take place, and in the growth zone these molecules will decompose at T_2 . After the decomposition, the transportation agent should diffuse back into the source zone. Thus, a fixed amount of the transportation agent may provide crystallization of arbitrary amount of the substance X [26]. Reaction used for the growth of ZnSe crystals may be written as



Detailed description of the crystal growth procedure and sample preparation may be found in [24], however, it should be mentioned that studied material was polycrystalline.

Luminescence in 420–800 nm range was excited by radiation of the pulsed nitrogen SRS NL100 laser with 337.1 nm wavelength, pulse energy of ~ 170 μJ , and registered by Hamamatsu R943-02 photomultiplier tube. The SRS 250 Boxcar Averager was used to integrate the signal from the photomultiplier tube. In middle-IR spectral range (800–3000 nm), a solid state YAG: Nd³⁺ laser (532 nm, ~ 300 mW) and PbS-based photoresistance Hamamatsu P394A were used. The spectra were analyzed with MS257 diffraction grid monochromator with resolution better than 1.3 nm. The input slit was covered with correspondent spectral filter to prevent registration of higher orders of the diffraction grids. The studied samples were mounted on the cold finger of the open cycle helium cryostat Janis Research ST-100. The magnetization of

the samples was measured with a Quantum Design MPMS XL highly sensitive superconducting quantum interference device (SQUID) magnetometer at temperatures of 5–300 K in the constant magnetic fields up to 5 T.

3. The energetic structure of V ions in II–VI compounds

Position of vanadium energy levels within the ZnSe bandgap was studied by both experimental and theoretical methods [5,9], but there are significant differences in positioning of various charge states and the energy distance between the levels [10]. The vanadium ion forms the cation substitution defect in ZnSe [5] as do all other TM ions in II–VI semiconductor compounds (e.g. [3,27]). Beside the neutral $\text{V}^{2+}\{3d^3\}$ state, the transitions involving participation of both acceptor $\text{V}^{3+}\{3d^2\}$ and donor $\text{V}^+\{3d^4\}$ states were observed in emission and absorption spectra [8–10]. However, only the positively charged V^{3+} state was observed in the EPR spectra [6]. The reason for the absence of the ground states might be line broadening caused by strain in connection with the expected Jahn-Teller distortion, even at the lowest achievable temperatures [7]. Excitation and sensitization experiments allowed to determine the positions of the ground V^{2+} state at 1.43 eV below the bottom of the conduction band and V^+ at 1.91 eV above the top of the valence band [7] (Fig. 1). However, this assignment is also disputable, e.g. V^{2+} level sometimes is reported to be placed at 1.92 eV below the conduction band [10], in this case 1.43 eV transitions should be associated with the V^+ level (Fig. 1, inset). Position of the vanadium acceptor state was detected at 0.62 eV above the valence band [28].

Detailed description of the splitting of the free vanadium ion energy states by the zinc selenide crystal field, as well as the splitting parameters, may be found elsewhere [5,6,10]. Here we will just briefly describe the experimental results of this splitting and the energy distance between the splitted levels. Intrashell emission was observed for all three possible charge states of the vanadium ion in ZnSe. The ${}^4\text{T}_2 \rightarrow {}^4\text{T}_1$ transitions within the V^{2+} ion are placed at 4350 cm^{-1} (~ 0.538 eV) [8], that is in a good agreement with the excitation energy of the ${}^4\text{T}_2$ state of 0.500 eV [9]. The sixfold splitting of the non-phonon emission in ZnSe: V^{2+} is observed at very low temperature and, thus, must be related to splitting of the ground state, which cannot result from a low-spin ground ${}^5\text{E}$ ground state but from a high-spin state ${}^4\text{T}_1$ [10]. The second excited state ${}^4\text{A}_2$ is considered to be at 1.085 eV above the ground state [6]. Intrashell transitions within the ${}^5\text{E}$ and ${}^5\text{T}_2$ levels of V^+ ion are observed at longer wavelengths about 3640 cm^{-1} (~ 0.451 eV). The structured spectra in this region are usually interpreted by Jahn-Teller coupling with $E_{JT} = 90\text{ cm}^{-1}$ [8]. The shape and detailed structure of the 5100 cm^{-1} (~ 0.631 eV)

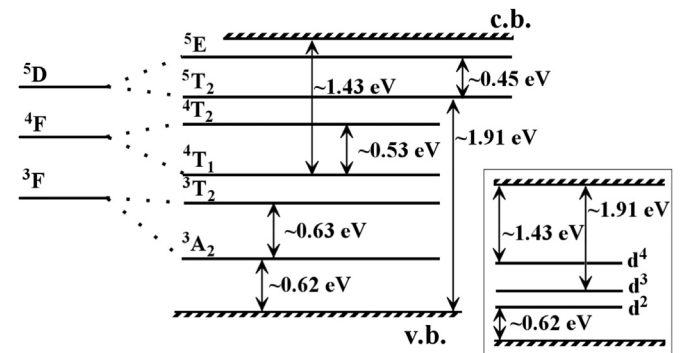


Fig. 1. The electronic energy levels of the vanadium free ion (left-hand side), and position of the vanadium ions energy levels within the ZnSe bandgap (right-hand side). Inset: alternative positions of the vanadium levels within the ZnSe bandgap.

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