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Magnetic and luminescent properties of nickel-doped ZnSe crystals

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ABSTRACT

Magnetic and photoluminescent properties of nickel-doped ZnSe crystals with impurity concentrations varied by changing the Ni amount in the source material from 0.001 to 0.50 at.% are studied in 5–300 K temperature range. Investigation of magnetic properties shows that Ni impurity in ZnSe forms isolated paramagnetic centers and probability of Ni–Ni pairs formation is negligible due to low Ni concentration in the samples. The contribution of Ni impurity to edge emission and its influence on infra-red emission are discussed. It is found that complete concentration quenching of luminescence within all studied spectral range is observed starting with Ni concentration of 0.50 at.%.

1. Introduction

Wide-bandgap semiconductors doped with magnetic impurities are of great interest and are widely studied due to their specific magnetic, optical, magneto-optical and magneto-transport properties. Materials with high temperature ferromagnetism and Curie point above the room temperature are required for use in spintronic applications. Potential candidates to be considered as magnetic dopants in II–VI semiconductors are the d-element impurities, such as Cr, Mn, Ni, Fe, Co, and V. Magnetic moments of transition metal d-electrons contribute to the ferromagnetic or antiferromagnetic ordering at temperatures below the Curie or Nèel point, respectively [1].

Since the nickel impurity is one of the prospective dopants for obtaining magnetic semiconductors, its behavior in various semiconductor compounds is widely studied. It was shown that, depending on environment and concentration, the doping Ni impurity contributes to superparamagnetic [2,3] or ferromagnetic [4,5] properties of the host material. For example, ZnO:Ni films, which are prospective for fabrication of integrated optical circuits and optical isolators based on magneto-optical effect, possess at low temperature (2 K) magnetization with the magnitude greater than theoretically calculated for paramagnetism of free Ni^{2+} ions. The difference between the theoretical and experimental curves of magnetization for ZnO:Ni samples increases with increasing temperature from 2 K to room temperature, thus, revealing the superparamagnetic nature of the sample magnetism. Moreover, the increase of Ni impurity concentration leads to the low-temperature stabilization of the magnetic phase in ZnO:Ni samples [2]. The superparamagnetic behavior was also observed in CdSb:Ni crystals, where Ni ions form nanocluster inclusions [3]. However, in granular Ni–SiO_2 and Ni–Al_2O_3 films, superparamagnetism was observed only at Ni concentrations above 50 vol.% [5]. At lower concentrations, the nickel impurity in these films forms isolated ferromagnetic clusters with a diameter of about 1–10 nm. The interaction of Ni ions with the nearest neighbors in $ZnCr_{1-x}Ni_xSe_4$ spinel is also ferromagnetic [4].

Investigation of the nickel impurity in II–VI wide-bandgap compounds is mainly focused on the study of optical end emission properties because of potential application of nickel-doped zinc chalcogenides in infrared (IR) solid state laser systems [6]. The fine structure of the zero-phonon emission line at 11,178 cm^{-1} in the near-IR photoluminescence (PL) spectra of ZnSe:Ni crystals, caused by $^3T_1$ (P) → $^3T_1$(F) radiative transition of $Ni^{2+}\{d^8\}$ ion in a tetrahedral crystal field, is reported in Ref. [7]. The IR PL spectra

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attributed to intrashell transitions of nickel ions in various compounds have been studied in detail in Ref. [8]. The influence of Ni concentration on visible and IR PL spectra of ZnSe:Ni crystals is also studied, the formation of the Ni impurity-bound excitons is suggested, and it is argued that recombination energy of the bound exciton is effectively transferred to d-band states of Ni ions affecting the PL associated with d–d transitions within Ni ions [9,10]. The interaction of nickel donor- and acceptor-bound excitons (DBE and ABE, respectively) with defect vibrations in ZnSe:Ni crystals is theoretically considered in Ref. [11]. Despite many recent works devoted to investigation of ZnSe:Ni optical properties, a number of questions on the charge state of nickel impurity and the possibility of nickel-based DBE and ABE formation are still open to discussion.

Magnetic properties of ZnSe:Ni crystals are practically not studied experimentally, while the theoretical studies show contradictory data. For example, theoretical investigation of ZnSe:Ni crystals magnetic properties [12] predicts semimetallic ferromagnetic phase due to the $d-d$ interaction of the Ni^{2+} ions by means of free carriers ($s-d$ interaction). These are in good agreement with the theoretical studies of spin-polarized electronic structure of the bands and magnetism in $Zn_{1-x}Ni_xSe$ crystals ($x = 0.25$), where nickel ions form a stable ferromagnetic phase [13]. However, the above-mentioned results are in contradiction with the prediction of spin-glass phase and antiferromagnetic interaction in ZnSe:Ni crystals [14]. Low temperature experimental investigation of magnetic properties of $Zn_{1-x}Ni_xSe$ diluted magnetic semiconductors (with a single concentration of $x = 0.0025$) has shown that the magnetic susceptibility at temperatures above 125 K is negative due to very low doping level and predominant diamagnetic contribution of ZnSe lattice to the total magnetization [15]. As the temperature decreases, the paramagnetic contribution of the localized spins of Ni^{2+} ions increases and, as a result, magnetization becomes positive. A low-temperature minimum in the magnetization versus temperature curve is observed for these crystals, and magnetization has paramagnetic character that was previously observed for $Zn_{0.95}Ni_{0.05}O$ powder [16].

In this paper, we present a comprehensive experimental study of magnetic properties of ZnSe:Ni crystals doped with various concentrations of nickel ions up to 0.50 at. %. Also, the influence of nickel impurity on magnetic properties of zinc selenide crystals is compared with Ni influence on PL properties of the samples.

2. Sample preparation and experimental techniques

Nickel-doped ZnSe crystals with various Ni concentrations were grown by chemical transport reaction technique. Iodine was used as a transport agent and nickel doping was performed during the growth of ZnSe crystals.

The concentrations of nickel in reactor were ranged from 0.001 to 0.50 at.%. The crystal growth temperature was 1170–1200 K, and the growth time was 10–14 days. Concentration of nickel impurity in samples (Table 1) was estimated from magnetization (see Section 4.1 for details) and optical absorption (Fig. 1) of the samples.

Table 1
Estimation of nickel concentration in the samples.

In reactor		From absorption		From magnetization	
at. %	10^{20} cm^{-3}	at. %	10^{20} cm^{-3}	at. %	10^{20} cm^{-3}
0.50	1.10	1.5	3.3	0.55	1.21
0.20	0.44	0.9	2.1	–	–
0.10	0.22	0.5	1.1	0.11	0.24
0.02(5)	0.05	0.2	0.4	–	–

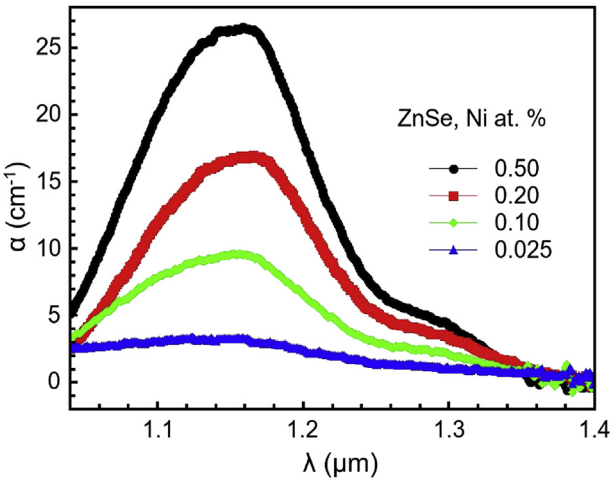

Fig. 1. Absorption spectra of Ni^{2+} ions in ZnSe:Ni samples.

Room-temperature absorption spectra were recalculated from the transmittance and a background subtraction was made to account for losses (e.g., light scattering) present in the sample. The concentration was obtained from the definition of the absorption cross-section $N=\alpha/\sigma$, where N is concentration, α is absorption coefficient and σ is absorption cross-section, considered $8.0\cdot10^{-20}$ cm^{-2} [6]. The difference between the concentration in reactor and that calculated from the absorption spectra may be caused by variation of the nickel ions absorption cross-section, for instance because of sensitization by iodine atoms. Interpretation of the nature of this result is beside the scope of this paper, however, it confirms that the nickel impurity incorporates into the ZnSe crystal lattice. In all the further discussion, nickel concentration in reactor will be considered.

The magnetic properties of ZnSe:Ni crystals were investigated using a SQUID (Superconducting Quantum Interference Device) magnetometer, model Quantum Design MPMS 5XL, at temperatures between 5 and 300 K in magnetic fields up to 5 T.

The PL spectra of ZnSe:Ni crystals were studied in the wavelength range of 430–3000 nm. The samples were mounted in a Janis Research gas-flow liquid helium cryostat working in the temperature range of 6–300 K. An ORIEL MS257 monochromator, a NL100 nitrogen pulse laser with a wavelength of 337.1 nm (3.68 eV) and Hamamatsu R943-02 photomultiplier were used for measurements in visible spectral range up to 800 nm. The SRS 250 Boxcar Averager was used to integrate the response of photomultiplier tube in a 9 μs range with a 1 μs delay after the laser pulse. A YAG:Nd^{3+} solid state laser (532 nm, ~ 300 mW) and Hamamatsu P394A PbS detector were used for 800–3000 nm spectral range.

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

The structure of Ni levels in $A^{II}B^{VI}$ compounds can be found elsewhere [6,17,18], and therefore we briefly describe the possible energy and charge states of nickel impurity in zinc selenide crystal host. The nickel ion replaces isoelectronically the group II atom in zinc chalchogenides and forms neutral Ni^{2+} {3 d^8} center [19,20]. The electron paramagnetic resonance investigations have shown that nickel can also exist in Ni^{3+} {3 d^7} and Ni^{+} {3 d^9} configurations in ZnSe [7,21]. Transitions between different charge states can also be observed in optical absorption [21,22] and emission spectra [23,24]. These measurements allowed to determine the positions of Ni energy levels within the ZnSe bandgap. However, designation of the charge-transfer process is not always unambiguous [22], which