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PHOTO-ESR STUDIES OF Ni DOPED ZnS AND ZnSe

M. SURMA, A.J. ZAKRZEWSKI, 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

The results of electron spin resonance experiments are presented for nickel doped ZnS and ZnSe. Energy level position of Ni^{1+} state in band gap of ZnS and ZnSe is determined. The nonradiative recombination processes of donor–acceptor pairs in Ni doped samples are discussed.

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1. Introduction

Transition metal impurities, such as iron [1, 2], chromium [2, 3], or nickel, belong to the most active centers of nonradiative recombination in wide band gap II–VI compounds [4, 5]. In this communication we present the results of electron spin resonance experiments performed under the photo-excitation (photo-ESR) for Ni doped ZnS and ZnSe. Nonradiative recombination processes in Ni doped samples are discussed. Efficiency of electron and hole trapping by Fe and Ni centers is compared. We verify also previous estimations of energy level position of Ni^{1+} center in ZnS and ZnSe.

2. Experimental

Photo-ESR experiments were performed on a standard X-band spectrometer. ZnS and ZnSe samples studied were grown by Bridgman method and were intentionally Ni doped in the range of 5×10^{16} to 1×10^{19} cm^{-3}. They were contamined with chromium, iron, copper and manganese. Some of ZnS crystals studied were co-doped with aluminium.

The Mn^{2+} magnetic resonance was observed before, under and after the photo-excitation of ZnS and ZnSe. This ESR signal was not photo-sensitive. ESR

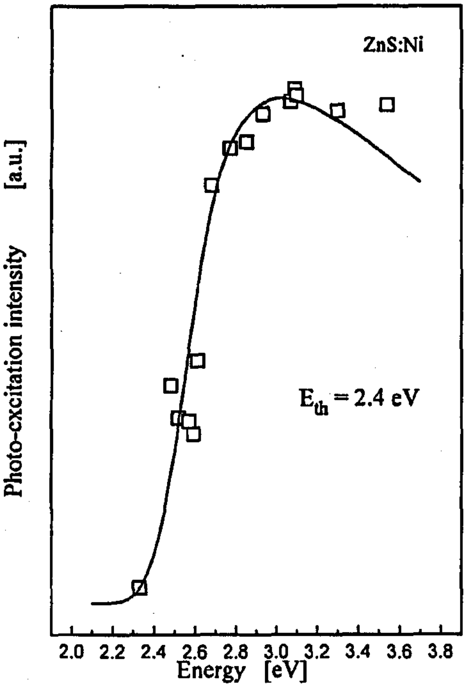

Fig. 1. Nickel 2+ → 1+ photoionization spectrum in ZnS, as derived from the photo-excitation spectrum of the Ni^{1+} ESR signal. The solid line presents the fit to the experimental results.

signals of Cr^{1+}, Fe^{3+}, Ni^{1+} and of unidentified signal with $g = 2.248$ were observed under the photo-excitation of ZnS. For ZnSe no Ni-related signal was detected in the ESR and only the Fe^{3+} magnetic resonance was observed under the illumination. The photo-excited ESR signals of Cr^{1+}, Fe^{3+}, Ni^{1+} remain metastable after turning off the light at low temperature. This enabled measurements of the photo-quenching spectra. In Fig. 1 we show the spectral dependence of the photo-excitation of Ni^{1+} and Fe^{3+} ESR signals in ZnS and in Fig. 2 the spectra of photo-excitation and photo-quenching of the Fe^{3+} ESR signal in ZnSe.

3. Discussion

Energy level position of Ni^{1+} in ZnS was determined from the fit to the observed photo-ionization band shown in Fig. 1. It was found that this level (i.e. 2+/1+) is located at 2.4 eV above the top of the valence band (VB), in agreement with some previous estimations [6–8]. Larger energy (2.545 eV) was derived from the recent photoluminescence (PL) excitation experiments [9]. The excitation spectrum of Fe^{3+} ESR signal was dominated by broad bands starting at 2.6 and 3.05 eV. Based on previous optically detected magnetic resonance (ODMR) experiments [10], these bands are related to acceptor → conduction band (CB)

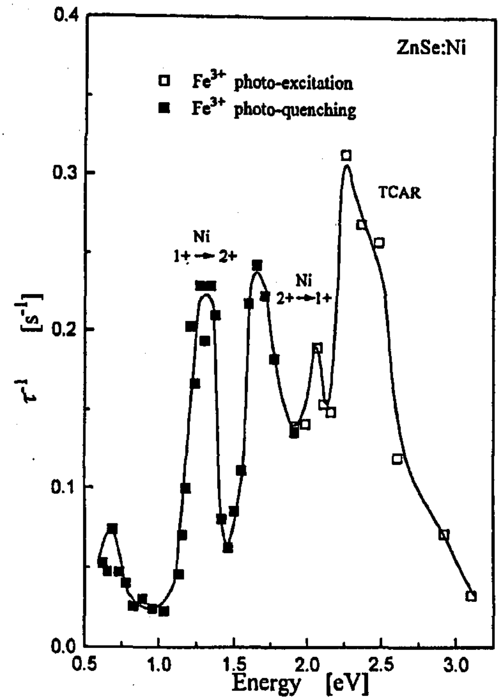

Fig. 2. Photo-excitation and photo-quenching spectra of the Fe^{3+} ESR signal in Ni doped ZnSe.

ionization transitions. The Fe^{3+} ESR signal is excited due to energy transfer from donor–acceptor pairs (DAPs) to iron, which is ionized [11]. Such process is called the three center Auger recombination [11] (TCAR). The TCAR process can be observed in ESR only if electrons excited in the CB do not readily recombine with iron Fe^{3+} centers. In previous ESR study the TCAR mechanism was observed for ZnS : Fe samples co-doped with chromium. The intense TCAR bands in the Fe^{3+} ESR photo-excitation spectrum in ZnS and ZnSe (Fig. 2) indicate thus that free electrons are efficiently trapped by Ni rather than by iron. The low energy band in the excitation spectrum of the Fe^{3+} ESR in ZnS is due to the Ni ionization transition. In this case the Fe^{3+} ESR is excited due to trapping of holes by Fe. Holes are generated in the VB in Ni (2+ → 1+) ionization transitions. The appearance of this band together with a lack of the Ni^{3+} magnetic resonance in the ESR spectrum indicates that iron 2+ can compete with nickel 2+ in hole trapping. The present ESR results indicate that the so-called bypassing [4, 5] process (subsequent electron and hole trapping by a deep center) is efficient for a nickel ion in ZnS, i.e., nickel is an efficient "killer" center of DAP processes in this material.

It is a quite common situation in photo-ESR investigations that ionization transitions of one center can be studied from the photo-sensitivity of another center [12]. This is also the case for Ni doped ZnSe samples. Even though Ni-related ESR signals were not observed, Ni ionization transitions can be studied from the photo-excitation and photo-quenching spectra of the Fe^{3+} ESR signal. These spectra are different from those observed by us for intentionally iron doped ZnSe [2]. Similarly, as in the case of ZnS, the ESR photo-excitation band is dominated by the TCAR process starting at 2.15 eV (Fig. 2). This indicates that also in ZnSe nickel must be a very efficient electron trap. The TCAR process was not observed in the ESR for samples intentionally doped with only iron. The lower energy band in the ESR photo-excitation spectrum and the one starting at 1.1 eV in the ESR photo-quenching spectrum (both shown in Fig. 2) were not observed in Fe doped samples. We relate them to the two complementary ($2+ \rightarrow 1+$ and $1+ \rightarrow 2+$) ionization transitions of Ni in ZnSe. The fit to the latter band locates the Ni^{1+} energy level at 1.1 eV below the bottom of the CB, in agreement with previous estimations from optical measurements [6–8].

Concluding, we have determined energy level position of Ni^{1+} $(2+/1+)$ charge state in the band gap of ZnS and ZnSe. Ni acts as an efficient "killer" of DAP PL. This work was partly supported by the grant no. 2 0469 91 01 of the State Committee for Scientific Research (Republic of Poland).

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