THE ESR SPECTRUM OF Mn^{2+} AND Eu^{2+} IN PBSE AND THESE CHANGE CAUSED BY IR LASER LIGHT

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1. Introduction

Potential practical applications of narrow-gap IV-VI semiconductor compound as infrared radiation sources and detectors, and thermoelectric generators, are the reason for the scientific interest in the mechanism of doping, in the impurity and defect states, and in their dependences on external agencies influencing such semiconductors.

Narrow-gap IV- VI - semiconductors grown from the melt or from the vapor phase suffer from the considerable concentrations of the metal and chalcogen vacancies ($N_m \sim N_{ch} \sim 10^{19}$ cm^{-3}), which are electrically active. Irrespective of the ratio of the components in the melt, the conditions during the technological processes ensure that the crystal matrix always contains regions which are rich in a metal or a chalcogen [1], and introduction of an impurity beginning from $N_{im} > 10^{18}$ cm^{-3} gives rise to additional fairly complex structure defects [2], which influence actively the electrophysical properties of this crystals [3,4].

It has been shown [3-5] that low-temperature infrared laser ($\hbar\omega < Eg$) «annealing» of IV- VI - crystals can after the carrier density, the carrier mobility, and the structural and optical properties.

The reported investigations were made on paramagnetic impurities (Mn, Eu) in the lattices of IV - VI - compounds and they showed that the impurity was located mainly in inclusions and at interstices. A characteristic feature of such crystals was the existence of anomalously low values of the mobility of free holes at helium temperatures.

Infrared laser radiation was found to increase the concentration of the manganese and europium impurities at the lattice sites and a combination of an electromagnetic laser radiation wave and a weak external electric field resulted in directional migration of the metal ions M^{2+} along the direction of the external field [4].

It should be pointed out that these investigations have been particularly thorough in the case of PbSnTe solid solutions. Much less work has been done on the behavior of the impurities and this is particularly true of the transition and rare-earth metals in PbSnSe solid solutions [6]. However, it is the paramagnetic impurities that make it possible to use the ESR method, which has proved so successful in studies of the structure of impurity centers, determination of their charge state and the position in the lattice, and in studies of the mechanisms of formation of complexes and doping.

We shall report the investigations of the behavior of the europium and manganese impurities in PbSe and of the influence of infrared laser radiation corresponding to the transparency range of their compound on the electrophysical properties and ESR in order to determine the charge state and the position of europium and manganese in the lattice.

2.\Samples and experimental methods

The PbSe:Eu(Mn) single crystals were grown by directed crystallization from the melt. The impurities were introduced into the melt and this concentration was varied over the range $N_i \approx 5 \text{ x } 10^{17} \div 2 \times 10^{19}$ cm $^{-3}$

The crystals had a p-type conductivity with a hole concentration P at liquid – N temperature of $(2 \div 5) \times 10^{18}$ cm^{-3} regardless of the impurity concentration.

The samples cut from the ingots were about $7 \times 1 \times 0{,}5$ mm^3 and oriented in <001> direction along their long side.

The crystals were exposed to infrared laser light of photon energy lower than the band gap, $\hbar\omega < E_g$, where E_g is the band gap of PbSe and $\hbar\omega = 0{,}118$ eV. The power density of the laser light reaching a crystal was less than the threshold power density corresponding to damage (or melting) of a sample. The temperature of PbSe:Eu(Mn) during such exposure to laser radiation did not exceed 150° C. Heat treatment under similar conditions and at the same temperature produced no significant changes in electrical properties.

Tne ESR of the PbSe:Eu(Mn) single crystals was carried out on a VARIAN E-12 apparatus in the 3 -cm wavelength range and at temperature of 20 - 300 K.

3. Results and discussion.

During the initial stage of such laser irradiation (for a period $t_{irr.} < 2h$) we found that the density of holes in PbSe:Eu(Mn) crystals decreased and an inversion of the type of conduction took place. The time needed to cause inversion was governed by the laser radiation power density, i.e., the direction of changes in the electrophysical properties was the same as in the case of the compound PbSnTe, but the rate of the changes was approximately an order of magnitude higher (for the same treatment conditions). In the n-type conduction state (after t_{irr}, > 2h), it was found that - in contrast to PbSnTe - the dependence of the carrier density on the duration of irradiation was more complex. The carrier mobility then changed by one or two orders of magnitude, depending on the previous history of a sample.

The observed changes could be due to dissociation (under the influence of laser radiation) of the complexes rich in the metal component and subsequent filling of the vacant sites in the metal sublattice of PbSe. This process should be accompanied by an increase in the concentration of isolated europium and manganese ions at the metal sites of PbSe, which in its turn should increase the ESR signal of the impurity.

In the case of PbSe:Mn crystals with an impurity content $5 \times 10^{17} < N_{im} < 5 \times 10^{18}$ cm^{-3}, which were not exposed to laser radiation, the ESR spectra consisted of six isotropic hyperfine structure lines with the half-width ΔH=13 Oe (curve 1 in Fig.l), typical of isolated Mn^{2+} ions in the lattice of IV-VI crystal and due to the interaction between the $3d^5$ electrons of Mn^{2+} with an intrinsic nuclear moment (I=5/2) of the ^{55}Mn isotope. In this case the constants of the spin Hamiltonian had the following values: $g = 2,0003 \pm 0,0005$ and $A = (65,95 \pm 0,2) \times 10^{-4}$ cm^{-1}, where A is the hyperfine structure constant.

Interaction of laser radiation with PbSe:Mn crystals resulted eventually in an increase in the integral intensities of isolated hyperfine structure lines in the ESR spectrum (Fig.2). In addition, six auxiliary isotropic lines appeared in the ESR spectra at higher values of the magnetic field (curve 2 in Fig.l), The intensity of each of the six lines, observed in unirradiated crystals, first rose slightly, reached saturation, and hen fell (curve 1 in Fig.2); these hyperfine structure lines were not observed in the n - type conduction region (curve 3 in Fig.l). The intensities of the additional six hyperfine structure lines then increased (curve 2 in Fig.2). The constants of the spin Hamiltonian for the additional six lines were as follows: $g = 1,9949 \pm 0,0005$, $A = (66,14 \pm 0,2) \times 10^{-4}$ cm^{-1}.

It should be pointed out that the half-width ΔH of the hyperfine structure lines then decreased considerably (ΔH = 8,5 Oe).

The appearance of the additional sextet of isotropic lines during the laser illumination of the crystals can be explained, as in the case of PbTe (Ref. 4), by the appearance of Mn^{2+} ions at lattice sites in the matrix of the PbSe crystal.

A detailed analysis of the ESR spectra showed that initially the Mn^{2+} ions occupied mainly interstices in the crystal and the appearance of the additional six isotropic lines due to exposure to laser radiation could be attributed to the appearance of the site Mn^{2+} ions, concentration of which has grown with increasing of bombardment time. The absence of the super-hyperfine interaction in the ESR spectra in the case of PbTe:Mn crystals [7] due to the interaction of the $3d^5$ electrons of Mn^{2+} with the nuclear moments of the Se isotope (I=1/2) in the first coordination sphere could be explained by the fact that the nuclear moment of the Se isotope is 1,5 times smaller than the nuclear moment of the Te isotope. In addition, the half-width of the hyperfine structure lines in PbSe:Mn is considerably greater than in PbTe:Mn and the super-hyperfine constants satisfy the condition $\alpha_{Se} < \alpha_{Te}$, so that the super-hyperfine structure of PbSe:Mn cannot be resolved at T = 20 K.

TheESR spectrum of original samples PbSe:Eu was composed seven fine - structure lines of low intensity (corresponding to S = 7*/2),* and each of them consisted of weakly resolved hyperfine structure lines.

The laser irradiation of PbSe : Eu increased considerably the intensity of the hyperfine structure lines and improved their resolution. The hyperfine structure was best resolved in the case of the strongest (due to the $-1/2 \leftrightarrow +1/2$) central line in the spectrum. Away from the center of the spectrum, the intensity of the fine-structure lines fell (the ratio of the intensities of these lines observed on increase in the field amounted to approximately 3:33:10:93:10:33:3, although the theoretical ratio of the components of the fine-structure lines should be 7:15:12:16:12:15:7) and the hyperfine structure became less resolved. When a magnetic field with the orientation H || <100> ($\Theta = 0$) was applied the solution of the fine-structure lines was the highest along the field scale. The ESR spectrum of the PbSe:Eu obtained using the magnetic field orientation H ||<100> is shown in Fig.3.

It should be pointed out that in the case of PbSe:Eu crystals a deviation of the magnetic field direction H from <100> resulted in a strong broadening of the hyperfine structure lines and reduced

their intensity. For this reason we were unable to determine the angular dependence of the ESR spectrum (in the range $\Theta = 0 - 90°$) when the magnetic field was rotated in the (100) plane. The angular dependence recorded for PbSe:Eu in the range 0-30° was the same as the angular dependence of the ESR spectrum obtained for PbTe:Eu in Ref. 7, but the peak-to-peak amplitude of the ESR spectrum was considerably greater for H || <100> . Hence, we concluded that the angular dependence of ESR spectrum corresponded to the cubic symmetry of the impurity centers.

The existence of seven fine-structure lines corresponding to S = 7/2, and the angular dependence of these lines, indicated that the Eu impurity occupied the site position in the Eu^{2+} state. It is known that lead selenide has the NaCI structure and the point symmetry of the sites is O_h . The ionic radius of Eu^{2+} is somewhat less than the ionic radius of Pb^{2+}, so that there is no significant distortion of the immediate environment as a result of replacement of the host atom with the impurity at the regular sites, which was confirmed by the angular dependence of the spectrum. In the case of the point symmetry O_h the spin Hamiltonian for the Spin S = 7/2 is [9]

$$H = g\, \beta\, H\, S + b_4\, O_4 + b_6 + O_6 + A\, S\, I \quad (1)$$

The main ground term of the Eu^{2+} ion is $^8S_{7/2}$ ($4f^7$ configuration), which splits into two doublets (A_6 and A_7) and a quartet (A_7) under the influence of the spin-orbit and spin-spin interactions, and of the cubic crystal field. Depending on the sign and the values of the constants b_4 and b_6, the A_6 or A_7 doublet may be the lowest.

An investigation of the temperature dependence of the intensities of the ESR lines enabled us to establish the sequence of the energy levels and the signs of the spin Hamiltonian constants,

A detailed analysis of the results obtained allowed us to interpret all the lines in a spectrum and to identify the ESR hyperfine structure lines due to ^{153}Eu and ^{151}Eu.

Figure 4 shows a fragment of the ESR spectrum of PbSe:Eu in the region of the central group of the lines due to the -1/2 ↔ +1/2 spin transition.

In the case of an arbitrarily oriented magnetic field the energy levels could be found from Eq. (1) by diagonalization of the 8 x 8 matrix. For some orientations, for example, H || <100>, the energy levels of the spin Hamiltonian (1) could be obtained in an analytic form [9].

The observed ESR spectrum of Eu^{2+} in PbSe was described satisfactorily by assuming the case of a strong magnetic field with the following transition frequencies:

$$-1/2 \leftrightarrow +1/2 \qquad \hbar\omega = g\, \beta\, H_0,$$

$$\pm 7/2 \leftrightarrow \pm 5/2 \qquad \hbar\omega = g\, \beta\, H_0 \pm 20\, b_4\, p \pm 6\, b_6\, q$$

$$\pm 5/2 \leftrightarrow \pm 3/2 \qquad \hbar\omega = g\, \beta\, H_0 \pm 10\, b_4\, p \pm 14\, b_6\, q$$

$$\pm 3/2 \leftrightarrow \pm 1/2 \qquad \hbar\omega = g\, \beta\, H_0 \pm 12\, b_4\, p \pm 14\, b_6\, q$$

where $p = 1 - 5\Phi$, $\Phi = \zeta^2 m^2 + m^2 n^2 + b^2 n^2$, $q = 21/2\, (11\, \zeta^2 m^2 n^2 - \Phi + 2/21)$, and ζ,, m, n are the direction cosines of the field H_0 described in terms of the crystallographic axes.

The ESR spectrum obtained for H || < 100> at T = 20 K was used to find the constants of the spin Hamiltonian of Eq. (I):

$g = 2.0231 \pm 0.0005$;

$b_4 = (92.8 \pm 2.0) \times 10^{-4}\ \mathrm{cm}^{-1}$; $b_6 = (3.8 \pm 2.0) \times 10^{-4}\ \mathrm{cm}^{-1}$;

$A(^{153}\mathrm{Eu}) = (29{,}0 \pm 0.2) \times 10^{-4}\ \mathrm{cm}^{-1}$; $A(^{151}\mathrm{Eu}) = (12.7 \pm 0.2) \times 10^{-4}\ \mathrm{cm}^{-1}$. The ratio of the hyperfine constants $^{153}A : {}^{151}A$, obtained from our experimental data, was equal to the ratio of the magnetic moments of these two isotopes. An increase in the hyperfine structure constants of the Eu ion in PbSe relative to PbTe (Ref. 7) indicated an increase in the ionic binding of PbSe compared with PbTe.

4. Conclusion.

Our investigations thus demonstrated that the europium and manganese impurity occupies the site positions in the PbSe lattice and is in the Eu^{2+} (Mn^{2+}) state, and that it can also occupy interstices and form clusters. Moreover, like the Mn and Eu impurities in PbTe, it behaves as a "pseudo-donor". Laser irradiation ($\hbar\omega < E_g$) results in dissociation of electrically neutral inclusions containing the metal component and this is followed by filling of the vacant sites in the metal sublattice of lead selenide by ions of the components of the host crystal and of the impurity.

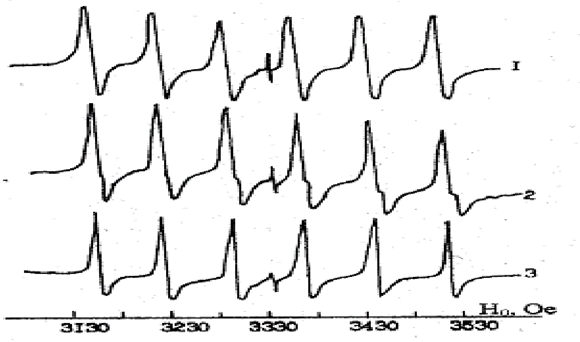

Fig. 1

Explanatory statement

Fig.1. ESR spectra of Mn^{2+} in PbSe ($W=25\ W/cm^2$):

1 – before laser radiation;

2 – after 30 min. irradiation;

3 – after 4,5 h. irradiation.

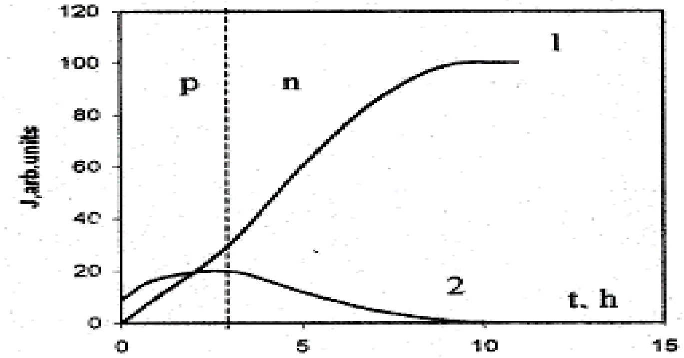

Fig.2

Fig.2. Dependences of the intensities (I) of thr ESR lines of Mn^{2+} in PbSe on the duration of laser irradiation: 1. – Mn^{2+} in lattice site: 2 - Mn^{2+} in intersitial position (W = 25 W/cm^2).

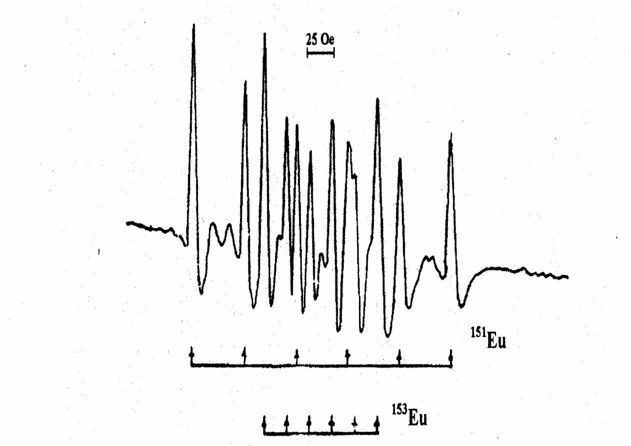

Fig. 3

Fig.3. ESR spectrum of Eu^{2+} in the case of PbSe recorded in a magnetic field directed along the <100> axis.

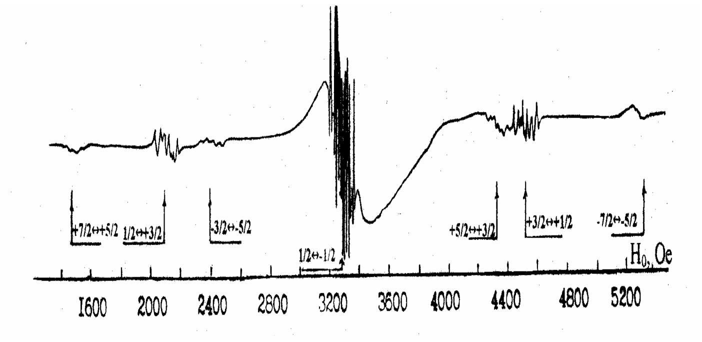

Fig.4

Fig.4. Fragment of the ESR spectrum of Eu^{2+} in the PbSe corresponding to the + 1/2 – 1/2 transition.

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