T.A. PROKOFIEV, A.V. IVANCHENKO

Oles Honchar Dnipro National University
(72, Gagarin Ave., Dnipro 49010, Ukraine; e-mail: tichonprok@yahoo.de)

EFFECT OF DISLOCATION HINDERING DURING PLASTIC DEFORMATION ON THE PHOTOLUMINESCENCE OF Mn²⁺ IONS IN ZnS SINGLE CRYSTALS

Experimental photoluminescence spectra of Mn^{2+} ions in single-crystalline ZnS specimens under various plastic deformations have been studied. Features in the photoluminescence spectra of specimens destroyed at small deformations are found. By resolving the spectra, individual spectral bands caused by the emission of Mn^{2+} ions with different local environments in ZnS single crystals subjected to various plastic deformations are obtained. Changes in the fraction of emitting Mn^{2+} ions in ZnS single crystals owing to changes in the plastic deformation magnitude are calculated for each individual band. A new individual band with a maximum emission at $\lambda_{\max} \approx 588$ nm is identified, and an explanation is proposed for the mechanism of its appearance at the displacement, hindering, and stopping of partial dislocations in the course of plastic deformation.

K e y w o r d s: photoluminescence, Mn^{2+} ions, ZnS single crystals, plastic deformation, spectrum resolution.

1. Introduction

Plastic deformation (PD) is known to result in a crystal structure reorientation of ZnS single crystals with an admixture of Mn^{2+} ions from the microtwins and polytypes to the unidirectional cubic sphalerite structure [1–6]. This process appreciably affects the radiative properties of indicated single crystals. Plastic deformation is accompanied by changes in the quantum-mechanical interaction between Mn^{2+} ions and the crystal lattice of ZnS single crystals. The dislocation motion can modify the nearest environment of manganese centers (MCs). As a result, conditions required to excite their radiation emission considerably change toward both facilitation and complication [7,8]. In most cases, a small burst of the radiation intensity takes place at the initial PD stage, when dislocations become shifted from their growth positions,

overcome the action of the compensating field created by the positive charge of the Reed cylinder, and undergo the action of the negatively charged components of Cottrell impurity atmospheres [7–9]. Then, as the PD processes develop further, the intensities of individual bands decrease at different rates until the physical destruction of deformed single crystals occurs [8]. As a result, the intensity of the total experimental spectrum decreases, with the maximum being shifted by 5–7 nm toward long waves.

Before the deformation, photoluminescence (PL) excitation conditions were not favorable for all Mn^{2+} ions in ZnS single crystals, because the amount of luminescent Mn^{2+} ions in those crystals does not exceed 1% of the total number of all MCs [10]. Therefore, the modification of these conditions in the course of the PD process changes the quantitative ratio between the radiative and non-radiative MCs. Simultaneously, the ratios between the radiative MCs with different

types of local symmetry also change. Additionally, as a result of the uncontrolled defect structure, the motion of dislocations can lead to the formation of new types of local symmetry for MCs in deformed ZnS crystals.

It should also be taken into account that it is quite difficult to predict the PD process experimentally. The impossibility to obtain even two completely identical specimens with the same defect structure almost always leads to the situation where the same deforming force results in absolutely different PD values in various specimens.

All the above changes and peculiarities reveal themselves in the variations of the shape, maximum position, and maximum intensity in the PL spectra of researched single crystals [7–10]. The aim of this work was a detailed analysis of those variations.

2. Experimental Specimens and Methods

ZnS single crystals with the admixture of Mn^{2+} ions were studied. They were grown from a melt using the Bridgman–Stockbarger method at the temperature $T = 2073$ K and under an argon pressure of about 150 atm.

According to X-ray diffraction analysis, ZnS single crystals had a cubic structure of Td symmetry, and they contained a large number of various defects [11], which gave rise to the formation of a microtwin structure. The existence of blocks was found. The blocks were the regions of single crystal disoriented with respect to one another by 2° and separated by dislocation walls. According to the data of emission spectral analysis, "pure" ZnS single crystals contained Al, Ti, Fe, Mn, Mg, and Cu impurities in concentrations not exceeding 10^{-5} g MnS/g ZnS (g/g). All examined specimens were obtained by chipping the larger blocks of single crystals along the cleavage plane, i.e., in parallel to the (111)C axis, and their subsequent mechanical treatment, grinding, and polishing.

The polished specimens before their deformation were $1.8 \times 1.8 \times 8.6$ mm³ in size. The deforming stress was applied at an angle of 45° to the sliding (111)C plane. The PD procedure was performed at the temperature $T = 423$ K and a deformation rate of about 5×10^{-8} m/s. The PL spectra were registered after every stage of specimen deformation.

The experimental PL spectra of Mn^{2+} ions in ZnS single crystals represent the total radiation of several overlapping luminescence bands. Each of them is associated with the radiation emission of MCs with a certain local symmetry. The type of local symmetry associated with each MC band, the number of bands, and the positions of their maxima were described in works [10, 12–15]. Accordingly, the individual PL band with the maximum at $\lambda_{\max} = 557$ nm was associated with the emission of Mn^{2+} ions located at stacking faults with the local symmetry C_{3v} (sites of the AS and PN types) and in the field with the cubic local symmetry Td (sites of the AN type) [10,12]. The individual PL band at $\lambda_{\max} = 578$ nm was associated with the radiation emission of MCs located near dislocations and point defects [12–14]. The individual band with the maximum at $\lambda_{\max} = 600$ nm is related to the radiation emission of MCs located in the cubic local environment in the octahedral interstitials [12, 13, 15]. Finally, according to the results of work [15], the individual band at $\lambda_{\max} = 635$ nm was emitted by the α-MnS phase impregnated in ZnS.

Proceeding from those facts, in order to trace the processes occurring during PD and their effect on PL of Mn^{2+} ions with various local environments in ZnS single crystals, and to relate the detected changes in the PL spectra to the changes in the crystal lattice of ZnS single crystals, it was necessary to resolve the experimental PL spectra into individual components and trace their modifications under various excitation conditions. In this work, the method of resolution into individual components was used (it was also applied in works [8, 16], while analyzing the same single crystals). The method allowed us to identify individual bands provided that their number and maximum positions are known. We also used this method to analyze the luminescence spectra, which allowed us to identify earlier unknown bands (i.e., without any *a priori* information concerning the positions of their maxima, half-widths, and number) that turned out weakly pronounced or strongly overlapped by neighbor individual bands, which were described in work [17].

3. Experimental Results

Practically no differences were detected between the PL spectra of various specimens before the plastic deformation. In most cases (in approximately 90% of the experiments), the low application rate of a deforming force together with experimentally se-
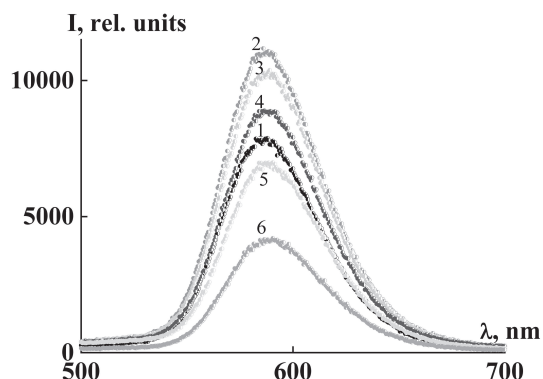
I, rel. units

Fig. 1. Experimental PL spectra of Mn^{2+} ions in ZnS single crystals at various PD values: $\varepsilon = 0$ (*1*), 1.4 (*2*), 4.22 (*3*), 8.8 (*4*), 17.96 (*5*), and 25% (*6*)
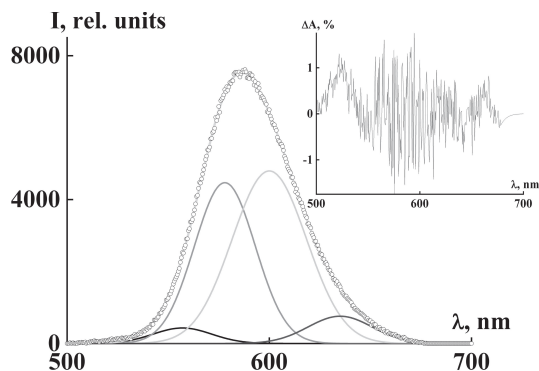

Fig. 2. Resolution of the PL spectra of ZnS:Mn single crystals into individual bands with $\lambda_{max} = 557$, 578, 600, and 635 nm. $C_{Mn} = 10^{-2}$ g/g, $\lambda_{exc} = 408$ nm, and $\varepsilon = 0$. The experimental total PL spectrum is exhibited by points, and the calculated intensity functions for resolved PL bands, as well as their sum, by curves. The function describing the deviation ΔA of the envelope of the sum of resolved peaks [8] from the experimental spectrum is shown in the inset

lected geometric dimensions of the deformed specimens allowed us to obtain rather large PD values, ε, before the specimen underwent the physical destruction. The ε values reached magnitudes of 25–27% [8]. With the help of the method applied in works [8, 16], the spectra obtained in those studies were successfully resolved into four individual bands, which were described above. These results allowed us to construct quite an adequate model of radiating MCs in the course of PD process for each individual band (see Figs. 1 and 2).

It was found that, in approximately 10% of examined cases, the specimens were destroyed at relatively small PD values, $\varepsilon \approx 5$–7%. Their PL spec-

tra (Fig. 3, *a*) contained specific features that could not be explained only as a result of the poor preparation of the specimens, their treatment, or experimental errors. Most clearly, these features were detected in the specimens with the PL excitation wavelength $\lambda_{exc} = 396$ nm and the manganese concentration $C_{Mn} = 10^{-2}$ g/g at the liquid nitrogen temperature $T = 77$ K. Attempts to resolve the corresponding spectra into four known individual bands did not allow us to obtain sufficiently adequate quantitative models of MC radiation emission in ZnS single crystals because the spread of deviations of the sum of individual bands from the experimental spectral values in the wavelength interval studied in work [8], which is associated with the radiation emission by Mn^{2+} ions, was about 10% (Fig. 3, *b*).

Taking into account that the applied method provided quite acceptable results in the other 90% of studied cases, it was suggested that this error arose due to the influence of other factors on the resolution accuracy of four known individual bands from the experimental spectrum. One of the factors is the possibility that 10% of PD experiments comprise atypical cases where there arises one more individual band with an unknown position of its maximum, which can be poorly detected and strongly overlaps with the neighbor bands. In order to resolve it, we used the method presented in work [17]. As a result, we determined the coordinates of the maximum of an earlier unknown band, $\lambda_{max} \approx 588$ nm, and resolved the atypical PL spectra into five individual bands using the method presented in works [8, 16]. The results obtained allowed us to construct a model that describes changes in the radiation of individual bands associated with the radiation emission by MCs with different local symmetries in ZnS single crystals during PD. The spread of error values in the wavelength interval, where the radiation emission of Mn^{2+} ions in ZnS single crystals was registered, did not exceed 1.8% (Fig. 3, *c*). The changes in the calculated individual bands are illustrated in Fig. 4.

It should be noted that the maximum located near 588 nm could be clearly detected in the plot of the error function ΔA only at a deformation of 4.3% (i.e., immediately before the destruction). The resolution of the spectra registered at smaller deformations into individual components was carried out after this detected maximum was taken into consideration.
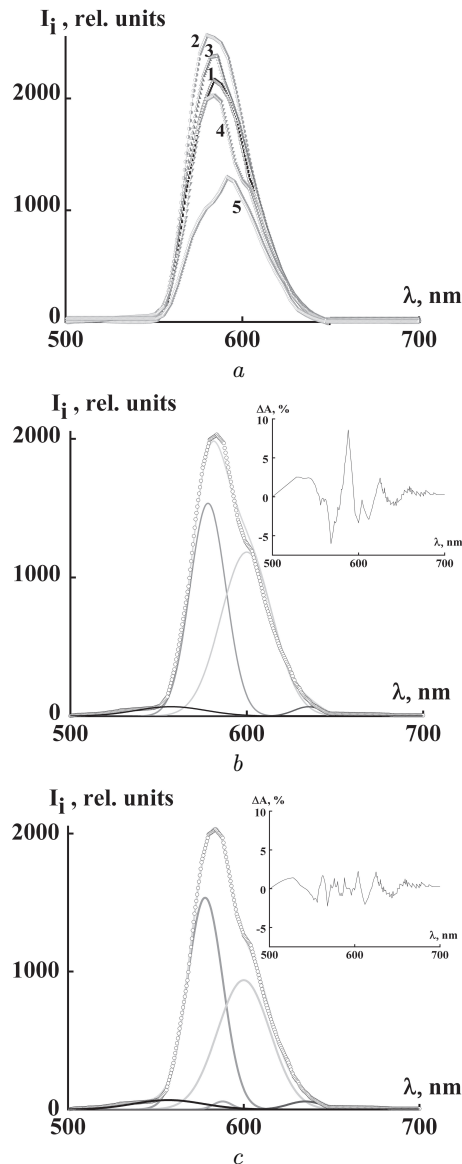
Fig. 3. Atypical experimental PL spectra of Mn^{2+} ions in ZnS single crystals at various PD values: $\varepsilon = 0$ (*1*), 1.57 (*2*), 1.8 (*3*), 4.33 (*4*), and 6.4% (*5*) (*a*) and their resolutions into 4 (*b*) and 5 (*c*) bands at $\varepsilon = 4.33\%$. $\lambda_{exc} = 396$ nm and $C_{Mn} = 10^{-2}$ g/g. The experimental total PL spectra are exhibited by points, and the calculated intensity functions for individual PL bands, as well as their sums, by curves. The functions describing the deviation ΔA of the envelope of the sum of resolved peaks from the experimental spectra are shown in the insets

Fig. 4. Resolved bands of atypical PL spectra of Mn^{2+} ions in ZnS single crystals at various PD values: $\varepsilon = 0$ (*1*), 1.57 (*2*), 1.8 (*3*), 4.33 (*4*), and 6.4% (*5*) (*a*). $\lambda_{exc} = 396$ nm and $C_{Mn} = 10^{-2}$ g/g. Corresponding scaled-up individual bands with $\lambda_{max} \approx 588$ (*b*) and 635 nm (*c*)

The individual band with $\lambda_{max} = 557$ nm was detected only at the value $\varepsilon = 4.3\%$ in the form of a wide Gaussian curve (Fig. 3). In all other measurements,

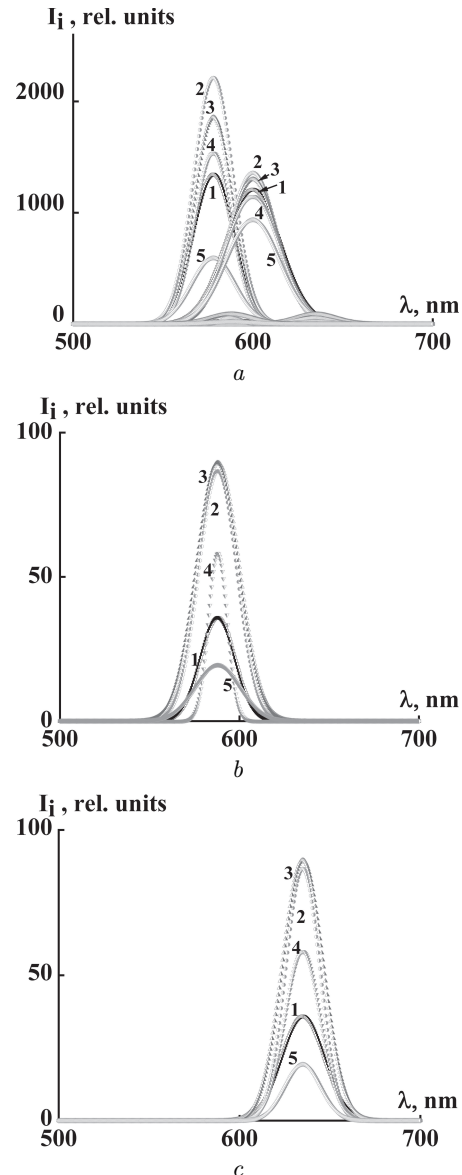its radiation intensity was almost zero. Therefore, it is not depicted in Fig. 4.

Unlike the results obtained in work [8], where the changes in individual bands were characterized by the areas under the corresponding spectral contours, the analysis of atypical cases in this work revealed sig-

Parameters of the resolved emission
bands of Mn²⁺ ions in ZnS single crystals calculated for various PD values

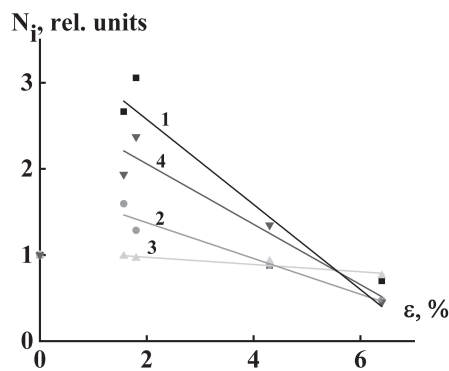| ε, %	$\lambda_{\max} \approx 588$ nm			$\lambda_{\max} = 578$ nm			$\lambda_{\max} = 600$ nm			$\lambda_{\max} = 635$ nm		
	S_i	w_i	A_i	S_i	w_i	A_i	S_i	w_i	A_i	S_i	w_i	A_i
0	866.3	22.7	35.9	37838.8	26.5	1343.0	46148.7	35.9	1208.0	1060.2	27.8	35.9
1.57	2308.2	25.0	86.7	60337.7	25.6	2212.0	45579.6	31.5	1359.0	2051.4	22.2	86.7
1.8	2648.1	27.8	89.6	48692.2	24.6	1859.0	44472.2	32.1	1302.0	2514.0	26.3	89.6
4.3	762.1	12.3	58.1	33512.0	22.2	1418.0	42858.6	35.1	1146.0	1428.7	23.1	58.1
6.4	606.1	29.4	19.4	17939.5	28.4	593.5	35102.0	35.2	936.9	477.6	23.2	19.4

Fig. 5. Dependences of the relative numbers N_i of luminescence centers (Mn²⁺ ions) in ZnS single crystals, which are associated with the emission of individual bands with $\lambda_{\max} = 588$ nm (*1*), 578 (*2*), 600 (*3*), and 635 nm (*4*), on the PD value ε, which were calculated by resolving the atypical experimental PL spectra. $\lambda_{\mathrm{exc}} = 396$ nm and $C_{\mathrm{Mn}} = 10^{-2}$ g/g

nificant changes in the band half-widths and amplitudes. Therefore, for more information, not only the areas under the spectral curves of individual bands are reported (they are proportional to the number of radiating MCs with a certain type of local symmetry, the integral brightness S_i) but also other results describing the changes of the band half-widths w_i and the maximum amplitudes A_i. The results are quoted in Table.

On the basis of this information, the changes in the relative numbers of luminescence centers (Mn²⁺ ions) with different local environments in the ZnS crystal lattice, which are associated with the emission of different individual luminescence bands, were calculated for various ε values. The relative number of corresponding luminescence centers N_i in undeformed single crystals was adopted as unity. The results obtained are shown in Fig. 5.

4. Discussion

The comparative analysis of the obtained results showed that the relative changes in the area, half-width, and amplitude of the peak turned out smallest for the band with $\lambda_{\max} = 600$ nm. The largest relative changes in the peak area and amplitude took place for the bands with $\lambda_{\max} = 558$ and 635 nm. Besides that, the band with $\lambda_{\max} = 558$ nm demonstrated the largest half-width fluctuations with a minimum at $\varepsilon = 4.3\%$. The character of changes in the integral brightness N_i somewhat correlates with the results of work [8], but the value of the ratio $\Delta N_i / \Delta \varepsilon$ is substantially different. In particular, for the band at $\lambda_{\max} = 558$ nm, this quantity is minimal at $\varepsilon = 4.3\%$.

Surely, there must be serious grounds for distinguishing new bands, because each of them does not exist independently, but is directly related to a certain number of emitting centers in the crystal lattice of the studied material, in our case, these are emitting Mn²⁺ ions with a certain local environment in ZnS single crystals. For undeformed single crystals, the set of such variants of local symmetry is well studied [10–15]. In our studies, their number, as a rule, remained constant for the majority of deformed crystals and was determined using a mathematical approach [8, 16]. In the examined atypical cases, the appearance of a new band correlated with the early destruction of specimens under small deformations, which was somewhat reflected in the PL spectra (see Figs. 3 and 4 and Table). In our opinion, the areas of "hindered dislocations" may appear in the deformed single crystals in this case. If the hindering occurs with the participation of radiating MCs, it should be observed in the PL spectra. This conclusion can

be explained by means of a detailed consideration of the motion of partial dislocations in ZnS single crystals.

If the magnitude of a deforming force is large enough, the dislocations become shifted from their initial positions and begin to move from the bulk to the surface of the single crystal. On its way, the dislocation encounters various obstacles that hamper its motion. Such obstacles may include various defects or Mn^{2+} ions themselves, because their ionic radius is larger than the radius of zinc ions. Since a partial dislocation is a linear defect, individual obstacles can exert a hindering effect, but it can be easily overcome. A different situation arises, if there are several such obstacles, and they are arranged in a line that is parallel to the dislocation itself, the so-called obstacle line. In this case, if the number of obstacles is enough, the dislocation motion can be stopped. In this case, the larger the number of obstacles in such a line, the higher the probability to stop the dislocation motion. It is most probable that such obstacle lines can be created by MCs that are located at the lattice sites and replace Zn^{2+} ions associated with emission of the band with $\lambda_{max} = 557$ nm, because their number is the largest in comparison with all other types of radiating MCs. Since the contribution of MCs with this type of local environment to radiation is minimal, it weakly manifests itself in the PL spectra. A large half-width of this line can be induced by a large variation in the number of MCs in the lines that hamper the motion of partial dislocations.

For the prolonged external mechanical stress, other dislocations begin to move in the layers located above or below the layer where the stopping took place. As in the previous case, this motion can also be stopped if the dislocations meet with a set of obstacles arranged in a line that is parallel to the dislocation itself, or the motion terminates in a natural way if the dislocation comes out to the specimen surface. Finally, there arises a situation when most dislocations come out to the surface or become slowed down in the bulk. A long-term application of a uniform deforming force to the surfaces of parallel faces gives rise to its nonuniform distribution in the bulk, which ultimately leads to the destruction of the deformed specimen.

Thus, our detailed studies of the PL spectra emitted by the specimens of ZnS single crystals with an admixture of Mn^{2+} ions, which are destroyed at low PD values $\varepsilon \approx 5$–7%, showed that the revealed specific differences are a result of the influence of the motion and hindering of partial dislocations on the variation in the nearest MC environment occurring during the PD process. It was shown that a new PL band with $\lambda_{max} = 588$ nm can be identified. In our opinion, it is associated with Mn^{2+} ions located at the octahedral interstitials which a partial dislocation has approached. The local symmetry of such MCs can vary owing to the motion of partial dislocations and their fixation in the vicinities of MCs. If the number of such arranged inline MCs becomes large enough, this can stimulate the early destruction of deformed single-crystalline specimens.

The indicated features in the arrangement of MCs, which affected the PL spectra, were atypical and inherent to approximately 10% of the studied specimens. In most cases, the number of MCs arranged in a line, which hamper the dislocation motion and can stop it, together with those MCs that affect the PL spectra, is insignificant so that the destruction of the specimens occurs at rather large PD values.

1. B.A. Abdikamalov, S.I. Bredikhin, M.P. Kulakov, V.S. Shekhtman, S.Z. Shmurak. Phase transition at plastic deformation of sulfurous zinc crystals. *Fiz. Tverd. Tela* **18**, 2468 (1976) (in Russian).

2. S.I. Bredikhin, S.A. Omelchenko, S.Z. Shmurak, N.A. Yakunina. EPR of Mn^{2+} in plastically deformed ZnS single crystals. *Fiz. Tverd. Tela* **23**, 903 (1981) (in Russian).

3. S.I. Bredikhin, S.Z. Shmurak. Luminescence and electrical characteristics of ZnS crystals undergoing plastic deformation. *Sov. Phys. JETP* **46**, 768 (1977).

4. S.I. Bredikhin, S.A. Omelchenko, S.Z. Shmurak. Change of charge states of centers in zinc sulfide crystals with dislocations. *Sov. Phys. JETP* **63**, 120 (1986).

5. *Electronic Properties of Dislocations in Semiconductors. Edited by Yu.A. Osipyan* (Editorial URSS, 2000) (in Russian).

6. S.A. Omelchenko, S.I. Bredikhin, P.A. Berlov, M.F. Bulanyi, S.Z. Shmurak, A.Ya. Yakunin. Kinetics of deformational reorientation of the structure of zinc sulfide and zinc selenide crystals. *Fiz. Tverd. Tela* **24**, 2803 (1982) (in Russian).

7. M.F. Bulanyi, A.A. Gorban', A.V. Kovalenko, B.A. Polezhaev, T.A. Prokof'ev, O.V. Khmelenko. Investigation of the photoluminescence of individual emission bands of Mn^{2+} ions in ZnS plastically strained single crystals. *Russ. Phys. J.* **45**, 1215 (2002).

8. T.A. Prokofiev, A.V. Ivanchenko, V.V. Gnatushenko. Luminescent analysis of ZnS:Mn single-crystal lattice changes during plastic deformation. *J. Appl. Spectrosc.* **86**, 213 (2019).

9. S.A. Omelchenko, M.F. Bulanyi, O.V. Khmelenko. Effect of the electric fields of immobile dislocations on photoluminescence and EPR in deformed ZnS crystals. *Phys. Solid State* **45**, 1688 (2003).

10. M.F. Bulanyi, A.V. Kovalenko, B.A. Polezhaev. Spectra of manganese emission centers in zinc sulfide. *J. Appl. Spectrosc.* **69**, 747 (2002).

11. A.Ya. Yakunin, I.V. Shtambur, A.S. Kushnir, S.A. Omel'chenko. Electron paramagnetic resonance (EPR) spectra of Mn^{2+} at normal and defect sites of a crystalline ZnS lattice. *Sov. Phys. J.* **16**, 1375 (1973).

12. H.E. Gumlich. Electro- and photoluminescence properties of Mn^{2+} in ZnS and ZnCdS. *J. Luminesc.* **23**, 73 (1981).

13. G.E. Arkhangelskii, N.N. Grigoriev, M.V. Fok, N.A. Yakunin. Influence of plastic deformation on luminescence and electron paramagnetic resonance of ZnS-Eu crystals. *Trudy FIAN SSSR* **164**, 43 (1985) (in Russian).

14. M.F. Bulanyi, B.A. Polezhaev, T.A. Prokof'ev. The nature of manganese luminescence centers in zinc sulfide single crystals. *Semiconductors* **32**, 603 (1998).

15. N.D. Borisenko, M.F. Bulanyi, F.F. Kodzhespirov, B.A. Polezhaev. Properties of emission centers in manganese doped zinc sulfide. *J. Appl. Spectrosc.* **55**, 911 (1991).

16. V.V. Gnatushenko, T.A. Prokofiev, O.V. Ivanchenko. *Photoluminescence Method for Analyzing Changes in the Structure of ZnS:Mn Crystals during Plastic Deformation.* Patent Ukraine No. 125082 dated April 25, 2018 (in Ukrainian).

17. T.A. Prokofiev, V.V. Gnatushenko, O.V. Ivanchenko. *Method for the Analysis of Experimental Luminescence Spectra.* Patent Ukraine No. 122574 dated December 10, 2020 (in Ukrainian).

Т.А. Прокоф'єв, О.В. Іванченко

ВПЛИВ ГАЛЬМУВАННЯ ДИСЛОКАЦІЙ
У ПРОЦЕСІ ПЛАСТИЧНОЇ ДЕФОРМАЦІЇ
НА ФОТОЛЮМІНЕСЦЕНЦІЮ ІОНІВ Mn^{2+}
В МОНОКРИСТАЛАХ ZnS

У роботі досліджено експериментальні спектри фотолюмінесценції іонів Mn^{2+} у зразках монокристалів ZnS для різних значень пластичної деформації. Виявлено особливості у спектрах фотолюмінесценції у зразках, що руйнуються при малих деформаціях. У результаті розкладання спектрів на індивідуальні складові одержано індивідуальні смуги, які зумовлені випромінюванням іонами Mn^{2+} з різним локальним оточенням у монокристалах ZnS при різних значеннях пластичної деформації. Розраховано зміни відносної кількості випромінюючих іонів Mn^{2+} у монокристалах ZnS при зміні величини пластичної деформації для кожної з одержаних індивідуальних смуг. У результаті розкладання виділено нову індивідуальну смугу з максимумом випромінювання при $\lambda_{max} \approx 588$ нм, а також запропоновано пояснення механізму її виникнення при переміщенні, гальмуванні і зупинці часткових дислокацій у процесі пластичної деформації.

К л ю ч о в і   с л о в а: фотолюмінісценція, іони Mn^{2+}, монокристали ZnS, пластична деформація, розкладання спектрів на індивідуальні складові.