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The Manifestation of Intracentral d^5-States of Impurity Ions in Luminescence of Zinc Oxide

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In 1992 it was for the first time discovered that in photoluminescence (PL) spectrum of ZnO narrow line A is observed at the energy of 1.7874 eV. This line was attributed to intracentral transition from the first excited state of Fe^{3+} ion to the ground state $^6A_1$ of d^5 -configuration of iron ion. It is natural to suppose that in PL and its excitation (PLE) spectra the other excited intracentral states can manifest themselves. In this paper in PL spectrum of ZnMnO single crystals at room temperature and excitation energies of 4.475 and 4 eV the thin structure of a previously known peak at the energy of 2.9 eV was discovered. One of the peaks of this thin structure at the energy of 2.56 eV is in a good agreement with $^4E \rightarrow {}^6A_1$ transition of Mn^{2+} ion, the following peaks can be attributed to transitions from the following excited states to $^6A_1$.

Keywords: Photoluminescence, zinc oxide, intracentral states.

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Introduction

In [1], in the photoluminescence (PL) spectra of the ZnO : Fe crystals, an intense line was found at 1.7874 eV that was called the *A*-line. The authors of this paper assign this line to the intracenter transition from the first excited state of the Fe^{3+} ion to the ground state $^6A_1$. That study did not consider the fact that, for the local environment of the impurity center of symmetry C_{3v} that occurs in zinc oxide, the first excited state appears to be ^4E, rather than $^4T_1$ as in the case for cubic symmetry. Line *A* observed in [1] was followed by several vibrational repetitions induced by lattice phonons, and, in addition, another intense peak corresponding to local vibration was observed at 1.723 eV. I.B. Bersuker in [2] provided the Tanabe–Sugano diagrams that are dependences of the energy level positions on the crystal field for various d^n-configuration options, including also for d^5, which is typical for the Mn^{2+} and Fe^{3+} impurity ions in II–VI : 3*d* compounds. According to this diagram, there are several types of excited intracenter states for the d^5-configuration. It would appear reasonable that these states also can appear in the PL and photoluminescence excitation (PLE) spectra.

This study makes an effort to find intracenter states of the d^5-configuration of the Mn^{2+} impurity ion in the II–VI : Mn compounds using ZnO : Mn as an example. Zinc oxide doped with 3*d*-metals is of interest for researcher because ferromagnetic ordering with the Curie temperature equal to several hundred degrees Kelvin was predicted in this compound [3]. In the GaAs : Mn compound where ferromagnetic ordering was first observed, the Curie temperature is much lower that room temperature [4], which greatly hinders practical application of this material. Moreover, zinc oxide with the 3*d*-type impurities may be potentially used for photosynthesis [5]. As uncontrolled impurity, our ZnO : Mn specimens contained the Fe^{3+} ions that were observed on the EPR signal spectra [6] and, as the Mn^{2+} ions, had the d^5-configuration. The Fe^{2+} state (d^6-configuration) is common for the Fe ion. Presence of the Fe^{3+} ions is explained as follows. The specimens were prepared by the hydrothermal method, whereby the liquid phase, besides the manganese and iron ions, also contained the lithium ions. Therefore, our specimens also contain the Li^+ ions negatively charged with respect to the lattice because they can give only one electron (not two electrons as the manganese and iron ions). Thus, one of the oxygen ions in the immediate environment of the Li^+ ion appears to be in the O^- state (rather than in the O^{2-} state). Due to high electronegativity, the O^- ion takes one electron from the Fe^{2+} ion and as a result the Fe^{3+} ions are formed.

Experimental conditions

The examined single-crystal $Zn_{1-x}Mn_xO$: Fe specimen was grown at the Institute of Solid State Physics (Chernogolovka) by the hydrothermal synthesis method developed by G.A. Emelchenko. The specimen had a $6 \times 3.5 \times 0.7$ mm rectangular parallelepiped shape with the crystallographic axis **C** perpendicular to the major face. Iron existed in the crystal as an uncontrolled impurity. Mn concentration $x = 0.0009$.

PL were studied at temperatures below room temperature using a developed spectroscopic unit [7–9] based on the optical cryogenic system and the Shamrock SR-303i-B (Andor, UK) spectrograph equipped with the Newton^{EM} DU970P-BV-602 CCD matrix. A LED with maximum luminescence at 372 nm (3.33 eV) was used as an excitation source. The specimen was placed in the cryostat so that the angle between the exciting beam and crystallographic axis **C** was equal to 90°. The luminescent signal was transmitted through the OS-11 light filter, spectrally decomposed by diffraction lattice with a groove density of 150 mm^{-1} and detected by a matrix cooled to 193 K. The spectrograph entrance slit width was 50 μm, integration time — 5 s, integrations for averaging — 30.

The cryogenic system included the Janis CCS-100/204N closed-cycle helium cryostat, HC-4E1 (Sumitomo, USA) compressor, Model 335 (Lake Shore Cryotronics, USA) temperature controller and HiCube 80 Eco (Pfeiffer Vacuum, Germany) vacuum station that provided pressurization below $1 \cdot 10^{-4}$ mbar during measurement. PL spectra in the region of Fe lines and localized Mn exciton lines were measured in the spectral range 1.5–1.95 eV at 7.3 K and 150 K.

PL excitation and luminescence spectra were measured using the Perkin Elmer LS55 spectrometer at room temperature. The PL spectra were recorded in the range of 350–650 nm (1.9–3.54 eV) with excitation in the 230 (5.39 eV), 277 (4.475 eV), 310 (4.0 eV) and 340 nm (3.646 eV) bands. Scanning rate was 60 nm/min. Excitation and recording monochromator slit width was 10 nm.

PL in the examined specimen was excited by the monochromatic nonpolarized light from a xenon lamp. PL spectra were recorded via linear polarizers. The specimen was placed in the LS55 spectrometer chamber so that light passing through the monochromator fell onto the major face of the specimen at 45°. Whereby the angle between the excitation beam falling on the specimen and the crystallographic axis **C** was also equal to 45°. For a vertical polarizer, the recorded light is polarized so that the light wave electric vector is perpendicular to the plane of incidence and, for the horizontal polarizer, the light wave vector is in the plane of incidence. According to the Malus law, the following expressions are derived for the recorded PL intensity:

$$I_h = (I_\sigma + I_\pi)/2$$

for horizontal polarization of incident light and

$$I_v = I_\alpha$$

for vertical polarization. In these equations, I_σ is the σ-polarization light intensity when the light wave electric vector **E** is perpendicular to the crystallographic axis **C**, and I_π is the π-polarization light intensity when vector **E** is parallel to **C**.

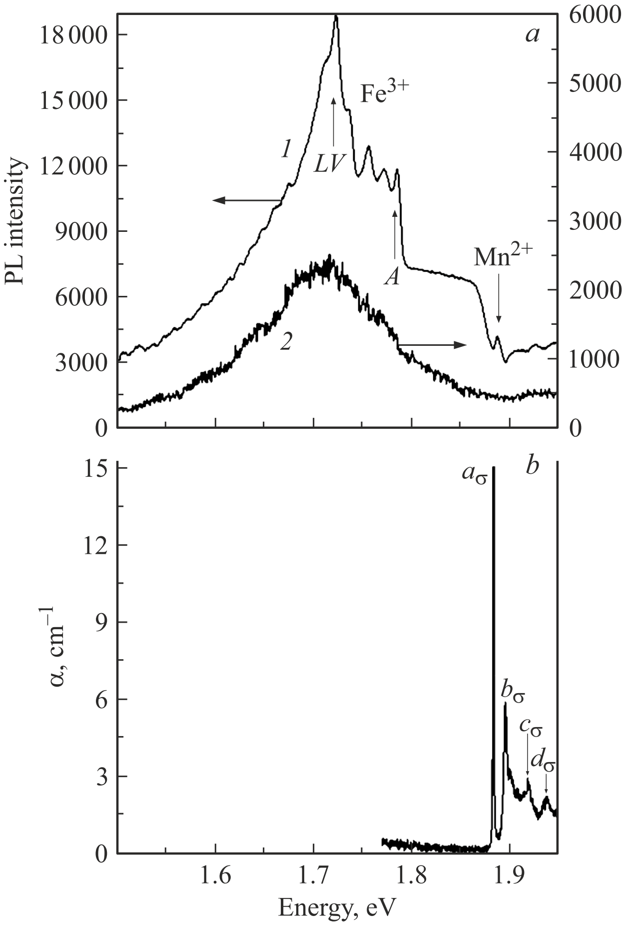

Figure 1. (*a*) PL spectra of ZnO:(Mn^{2+},Fe^{3+}) single-crystals in the spectral range of 1.5–1.95 eV at $T = 7.3$ (*1*) and 150 K (*2*). Excitation energy $E_{ex} = 3.33$ eV. (*b*) Optical absorption spectrum (α) of the ZnMnO:Fe^{3+} single-crystals for the incident light σ-polarization at $T = 4.2$ K [10].

Results and discussion

Figure 1, *a* shows the PL spectra of the ZnO:(Mn^{2+},Fe^{3+}) single-crystals in the spectral range of 1.5–1.95 eV at the temperatures of 7.3 K and 150 K. In the range of 1.72–1.79 eV at 7.3 K, the spectrum recorded in [1] is reproduced in the region of Fe^{3+} ion lines with the line *A*, series of vibrational repetitions of this line and local vibration intensive peak LV found in this study. At 1.884 eV and higher, several features corresponding to the lines of the exciton localized on the MnO$_4$ cluster is observed. For comparison, Figure 1, *b* shows the optical absorption spectrum in the area of the localized exciton lines from [10] for the σ-polarization of light falling on the specimen. These lines a_σ–d_σ are marked in the figure. However, a self-absorption effect occurs: luminescence induced by the exciton transition is immediately absorbed by the specimen. As a result of double Auger process, this energy is re-irradiated by the Fe^{3+} ion [11]. As the temperature increase up to 150 K, as shown in Figure 1, *a*, all these PL spectrum features disappear.

Figure 2 shows the PL spectra of the ZnO : (Mn^{2+},Fe^{3+}) single-crystals in another spectral range of 1.75−3.5 eV for the vertical and horizontal light polarizations at different excitation energies. These spectra were recorded at room temperature. As was previously known, the PL spectrum of Mn-doped zinc oxide contains two wide peaks with maxima at 2.1 eV and 2.9 eV. In [12], these two peaks were observed during investigation of nanopowders with crystal sizes of 30 nm at 86 K and excitation energy 3.64 eV. The first of these peaks is also observed in undoped ZnO specimens, it is induced by yellow-orange luminescence typical of this material. In case of Mn doping, this peak weakens. The peak at 2.9 eV is associated with the Mn impurity. In the ZnMnO single-crystals, these two peaks were also observed, but with another intensity ratio: in contrast with nanopowders, the peak 2.9 eV had much higher intensity than the peak 2.1 eV. In the PLE spectrum at 2.9 eV, intensity growth takes place in the area of interband transitions beginning from low values at $\hbar\omega \approx E_g$ with three well pronounces peaks at 3.9, 4.5 and 5.25 eV. The same effect was also observed in the $Zn_{1-x}Mn_xO$ ($x = 0.0016$) single-crystals [12]. Increase from low values of intensities of excitation spectrum with energy growth in the interband transition area is an unusual phenomenon: intensity in this area usually decreases. For comparison, in the $Zn_{0.9945}Mn_{0.0055}S$ single-crystals, a peak in the PL spectrum at 2.12 eV was known and was induced by the intracenter transitions of the Mn^{2+}ion ($^4T_1 \rightarrow {}^6A_1$) . The PLE spectrum contained peaks due to transitions into high-energy states of the Mn^{2+} ion ($^4T_2$ and $^4A_2$, ^4E). In the area of interband transitions, a maximum near E_g and gradual intensity decrease at $\hbar\omega > E_g$ are observed [13]. Therefore, in [12], to explain the peak 2.9 eV, an idea according to which this peak is caused by the high-energy intracenter transition of the Mn^{2+}ion was rejected. Instead of this another idea is proposed according to which due to hybridization of the *d*-states of the Mn^{2+} ion with the *p*-states of the nearest oxygen ions, the antibonding state *AB* split from the valence band top occurs in the energy band gap. This state, according to [12], similar to the system of intracenter states in $Zn_{0.9945}Mn_{0.0055}S$, forms a single system of levels with hybridized states V_1, V_2, and V_3 that show themselves through features in the PLE spectrum at 3.9, 4.5 and 5.25 eV. Transition of a hole from the state *AB* to the ground state gives a peak 2.9 eV in the luminescence spectrum.

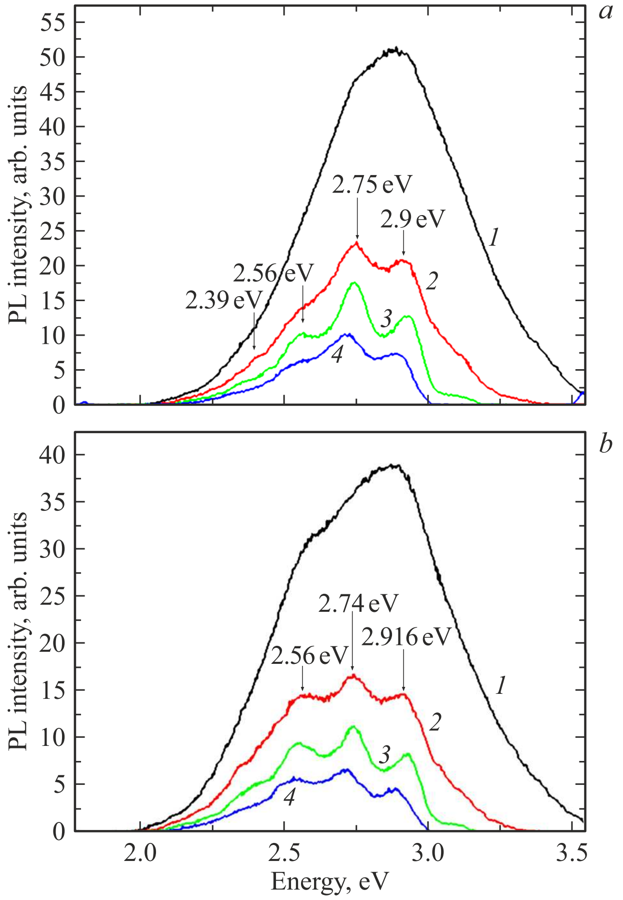

Figure 2. The PL spectra of the ZnO : (Mn^{2+},Fe^{3+}) single-crystals at room temperature in the range of 1.75−3.5 eV for the vertical (*a*) and horizontal (*b*) light polarizations. Excitation energy $E_{ex} = 5.39$ (*1*), 4.475 (*2*), 4 (*3*), 3.646 eV (*4*).

However, as shown in Figure 2, as fine structure of the luminescence peak 2.9 eV was detected in the PL spectrum of the ZnMnO : Fe^{3+} single-crystals at some excitation energy values. This structure was not observed earlier. This structure occurs both for the vertical and horizontal light polarizations, though with different peak intensity ratio. The peak of this structure at 2.56 eV adequately corresponds to the first excited state energy calculated in [14]. For the C_{3v}-symmetry that occurs for the impurity ion environment in zinc oxide, the type of this state is ^4E. In [15], Mn ion level positions in ZnMnO nanowires were determined from the time-delayed PL spectra. Peak at 2.75 eV may correspond to the state $^4A_2$. Near 2.9 eV, where the next peak is situated, according to [15], the state $^4A_1 + {}^4E\,(G)$ may occur. All these states are induced by splitting of the state ^4G in the symmetry field C_{3v}. At 3.1 eV in Figure 2, *a* (for vertical light polarization), an shoulder can be seen that is probably attributed to the state $^4E\,(F)$ arisen from splitting in the C_{3v}-symmetry field of the next excited state of the d^5-configuration — ^4F.

Near 2.39 eV on the curves in Figure 2, there are shoulders that can correspond to another state $^4A_2$ that is, according to [15], approximately in this region. And below this state, according to the same paper, there is one more state ^4E that may appear to be in the immediate vicinity of the energy of the exciton localized on the $Mn^{2+}{-}4O^{2-}$ cluster. In addition, the peak at 2.1 eV observed in [12] is not observed in Figure 2 probably due to high Mn concentration. But the luminescence peak 2.9 eV has an obviously asymmetric shape. On its low-energy edge that is exactly situated at 2.1 eV, there is an shoulder that apparently corresponds to the yellow-orange luminescence

Position of the Gaussian component peaks in the PL spectra of the $ZnO:(Mn^{2+},Fe^{3+})$ single-crystals for the vertical and horizontal light polarizations at the excitation energies $E_{ex} = 4.475$ and 4 eV

Vertical polarization		Horizontal polarization	
$E_{ex} = 4.475$ eV	$E_{ex} = 4$ eV	$E_{ex} = 4.475$ eV	$E_{ex} = 4$ eV
2.55188 eV	2.54249 eV	2.47436 eV	2.49394 eV
2.56295 eV	2.56996 eV	2.57054 eV	2.56064 eV
2.74797 eV	2.75059 eV	2.74226 eV	2.74363 eV
2.91422 eV	2.90774 eV	2.91941 eV	2.92011 eV
2.99911 eV	3.02254 eV	3.09704 eV	3.08812 eV

peak 2.1 eV observed in [12]. Another possible reason for weakening of this peak is the fact that the PL spectra in this region were recorded in this study at room temperature while in [12] they were recorded at 86 K.

A question may arise why there is no fine structure at the highest excitation energy $E_{ex} = 5.39$ eV. To understand the reason why there is not fine structure at such excitation energy, we'll use an equation for frequency distribution of light emitted by the atom in transition from the quasi-discrete excited level with the energy of $E_1 - i\Gamma_1/2$, where $\Gamma_1\ (= \Gamma_1/\hbar)$ is the total probability for all possible decays of this state per second [16], to the ground level with E_2, that is strictly discrete. This equation is written as [16]

$$dw = \frac{\Sigma|\langle\omega^2|\hat{V}|1\rangle|^2 d\omega}{(\omega_{12} - \omega)^2 + \Gamma_1^2/4}. \qquad (1)$$

In equation (1), dw is the probability of atom transition from the excited state to the stationary ground state in the frequency range $d\omega$, $\hat{V}$ is the operator of interaction between the atom and photon field, $\langle\omega^2|$ is the state with energy equal to $E_2 + \omega$, in which the atom is at the ground level and there is one quantum with the frequency ω, $|1\rangle$ is the initial state of the atom when it is excited to the state with the energy E_1, and there are not photons, $\omega_{12} = E_1 - E_2$ [16]. Summation in the numerator of the equation is performed over all polarization and photon motion directions. As can be seen from equation (1), the probability of photon emission has a sharp peak when condition $\omega_{12} \approx \omega$ is satisfied. However, in our experimental conditions, excitation frequencies differ considerably from ω_{12} that characterize the excited states of the Mn ions. Simple comparison on the basis of equation (1) for the probability of photon emission with 2.9 eV when the atom is excited by photons with 5.39 eV and 4.475 eV, respectively, shows that the energy decreases by a factor of 2.5 as the excitation energy grows. As a result of such radiation probability reduction, photons with the above-mentioned energy cannot be recorded when the Mn ion is excited by photons with 5.39 eV.

Figure 3 shows decomposition of the observed PL spectra into the Gaussian components at both polarizations for the excitation energies 4.475 eV and 4 eV. Positions of peaks of individual Gaussian lines are listed in the table or each case. This table shows that the positions of these lines for both polarizations are in good agreement.

For interpretation of the recorded spectra, Figure 4 shows the arrangement of intracenter states of the d^5-configurations of the Mn^{2+} and Fe^{3+} ions. As shown in [11], line A observed at 1.7874 eV is induced by the radiative recombination $^4E_1 - ^6A_1$ of the Fe^{3+} ion. Fe^{3+} ion transition to the excited state $^4E_1$ is induced by the Auger process associated with two impurity centers Mn^{2+} and Fe^{3+}. In particular, as a result of the Auger relaxation of the exciton that occurs on the $Mn^{2+} - 4O^{2-}$ cluster under the effect of light, the d^5-configuration of the Fe^{3+} ion, rather than of the Mn^{2+} ion, is excited [11]. Thus, the Fe^{3+} ion (d^5) appears to be in one of the excited states (this process is shown in Figure 4 by the thick horizontal arrow) and, as a result of nonradiative recombination, falls into the first excited energy state $^4E_1$. It is, as the adjacent state $^4A_1$ situated [11] near the localized exciton energy, occurs as a result of splitting of the state ^4G in the field of C_{3v} symmetry. The left side of Figure 4 shows transitions from the excited intracenter states of the Mn^{2+} ion to the ground state $^6A_1$ that induce the fine structure peaks of the observed PL spectra.

Thus, the found fine structure of the PL band 2.9 eV causes us to consider that the system of intracenter states of the Mn^{2+} ion also contributes to the luminescent properties of this compound. Positions of the peals of this fine structure make it possible to clarify the excited state level positions of the Mn^{2+} ion in ZnMnO with respect to the ground state $^6A_1$.

However, it should be noted that the obtained data is tentative. To prove the conclusions made in this study, further investigations of luminescence of the $ZnO:(Mn^{2+},Fe^{3+})$ crystals are required. specifically, it is necessary to examine the PL spectra of this compound at 2.9 eV and the PLE spectra in a wider temperature range.

Conclusion

Finally, the main results of the study shall be pointed out. In the $ZnMnO:Fe^{3+}$ crystals at room temperature and excitation energies of 4.475, 4 and 3.646 eV, PL band fine structure was found at 2.9 eV. Peaks of this structure are observed both at the vertical (corresponding to the σ-polarization) and at the horizontal (with the equal fractions of the σ- and π-polarizations of light) polarizations with different intensity ratio. These features may be understood as the manifestation of the intracenter states $^4E\ (G)$, $^4A_2\ (G)$ and $^4A_1 + {}^4E\ (G)$ of the Mn^{2+} ion in ZnMnO.

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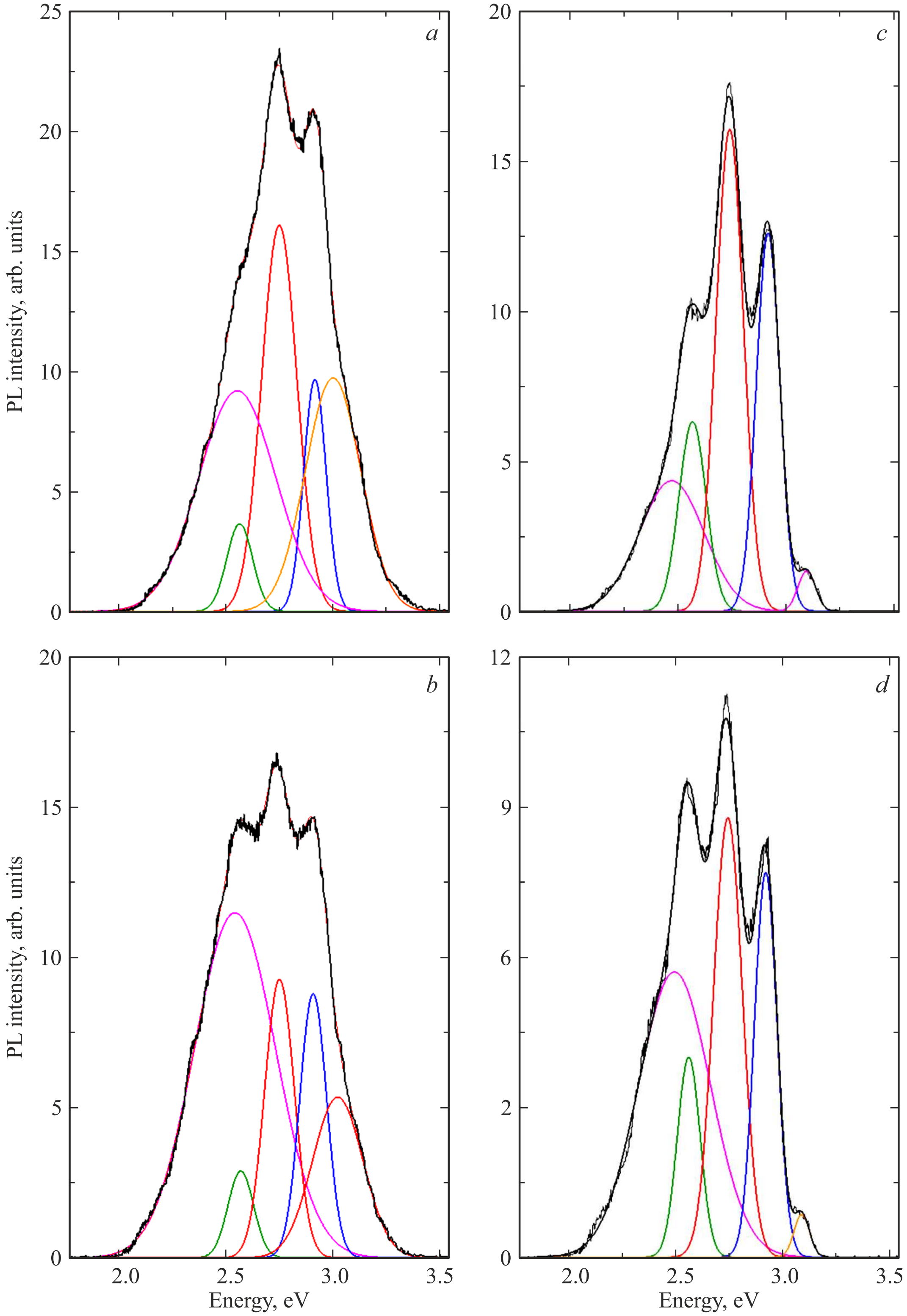

Figure 3. decomposition of the PL spectra of the ZnO:(Mn^{2+},Fe^{3+}) single-crystals for the vertical (*a, c*) and horizontal (*b, d*) light polarization at the excitation energies $E_{ex} = 4.475$ (*a, b*) and 4 eV (*c, d*) into the Gaussian components.

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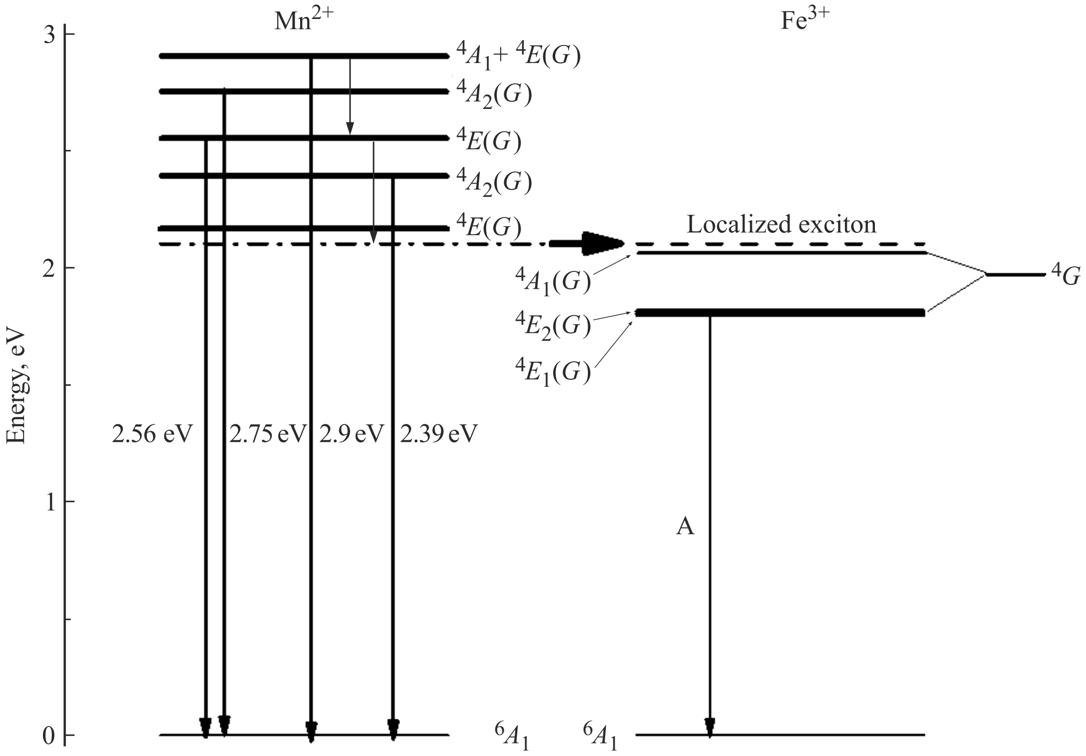

Figure 4. Diagram of the intracenter states of the d^5-configurations of the Mn^{2+} and Fe^{3+} ions.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] R. Heitz, A. Hoffmann, I. Broser. Phys. Rev. B, **45** (16), 8977 (1992).

[2] I.B. Bersuker. *Electronic structure and properties of transition metal compounds* (The University of Texas at Austin, 2010).

[3] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, D. Ferrand. Science, **287**, 1019 (2000).

[4] T. Ohno. Science, **281**, 951 (1998).

[5] M.R. Hoffman, S.T. Martin, W. Choi, D.W. Bahnemann. Chem. Rev., **95**, 69 (1995).

[6] V.I. Sokolov, N.B. Gruzdev, V.A. Vazhenin, A.V. Fokin, A.V. Korolev, V.V. Menshenin. J. Experimental and Theoretical Physics, **130** (5), 681 (2020). DOI: 10.1134/S1063776120040123.

[7] A.O. Shilov, R.V. Kamalov, M.S. Karabanalov, A.V. Chukin, A.S. Vokhmintsev, G.B. Mikhalevsky, D.A. Zamyatin, A.M.A. Henaish, I.A. Weinstein. Nanomaterials, **13** (14), 3109 (2023).

[8] S.A. Belyakov, A.S. Lesnichyova, M.S. Plekhanov, N. Prinz, M. Zobel, A.S. Vokhmintsev, I.A. Weinstein. J. Materials Chemistry A, **11** (36), 19605 (2023).

[9] S.S. Savchenko, A.S. Vokhmintsev, I.A. Weinstein. J. Lumin., **242**, 118550 (2022).

[10] V.I. Sokolov, N.B. Gruzdev, V.V. Menshenin, A.S. Vokhmintsev, S.S. Savchenko, I.A. Weinstein, G.A. Emelchenko. Opt. Spectrosc., **130** (12), 1538 (2022). DOI: 10.21883/EOS.2022.12.55239.3850-22.

[11] V.I. Sokolov, V.V. Menshenin, N.B. Gruzdev, A.F. Zatsepin. Phys. Solid State, **66** (2), 303 (2024). DOI: 10.21883/0000000000].

[12] V.I. Sokolov, A.Ye. Yermakov, M.A. Uimin, A.A. Mysik, V.A. Pustovarov, M.V. Chukichev, N.B. Gruzdev. J. Lumin., **129**, 1771 (2009).
N.B. Gruzdev, V.I. Sokolov, A.E. Ermakov, M.A. Uimin, A.A. Mysik, V.A. Pustovarov. ZhTF, **138**, 2 (261) (2010) (in Russian).

[14] T. Mizokawa, T. Nambu, A. Fujimori, T. Fukumura, M. Kawasaki. Phys. Rev. B, **65**, 085209 (2002). DOI: 10.1103/PhysRevB.65.085209

[15] R. Liu, L. Shi, B. Zou. ACS Appl. Materials and Interfaces, **6**, 10353 (2014).

[16] V.B. Berestetsky, E.M. Lifshits, L.P. Pitayevsky. *Kvantovaya elektrodinamika* (Nauka, M., 2) (in Russian).

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