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Fe^{3+} Center in ZnMnO

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In ZnO the impurity ion of iron which substitutes the zinc ion must be in the Fe^{2+} state (d^6 — configuration), but it often manifests itself as Fe^{3+} (d^5). In 1992 the narrow line A appearing as a result of intracentral transition of Fe^{3+} (d^5) ion in the photoluminescence (PL) spectrum of ZnO at the energy of 1.7874 eV was seen for the first time. This line was accompanied by the intensive vibrational phone which was caused by the ZnO lattice phonons. In this work significant differences between the PL spectrum of ZnMnO : Fe^{3+} and PL spectrum of ZnO : Fe^{3+} are shown. In PL spectrum of ZnMnO : Fe^{3+} line A is splitted into two components. Under the influence of light in ZnMnO : Fe^{3+} the exciton localized on $Mn^{2+}-4O^{2-}$ — cluster appears. The Auger relaxation of this exciton leads to the excitation of d^5-configuration of Fe^{3+} ion, not the Mn^{2+} ion. In our case the nonstandard Auger process with two impurity centers with $^6A_1$ ground states takes place.

Keywords: Photoluminescence, zinc oxide, Auger process.

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1. Introduction

Study of $3d$-metal impurities in semiconductors II–VI is aimed at searching for magnetic ordering in these materials. The zinc oxide doped with $3d$-metals is of particular interest, following the theoretical prediction of ferromagnetic ordering with a Curie temperature of several hundred degrees Kelvin [1]. The potential possibility of this material use for photosynthesis further increases the applied interest in it [2].

For the first time, ferromagnetic ordering was observed for GaAs : Mn [3]. But Curie temperature was significantly lower than room temperature. This makes the practical use of GaAs : Mn difficult. Considerable efforts to obtain magnetic ordering were directed toward II–VI compounds doped with manganese. In ZnTe and CdTe compounds the solubility of manganese reaches 60–70%, but magnetic ordering does not appear.

Various doping options for II–VI compounds (nickel, manganese, cobalt, iron) resulted in the appearance of some physical properties that are of interest for studies. A compound with such properties turned out to be zinc oxide doped with iron. In II–VI crystals the ions Fe^{2+} replacing the ions Zn^{2+} shall have the configuration d^6. ZnMnO : Fe crystals were obtained by the hydrothermal method. Lithium compounds were present in the liquid phase. Therefore, ZnO crystals contain ions Li^+, negatively charged relative to the lattice, since they can give only one electron to oxygen ions. Thus, in the immediate environment of the ion Li^+ one of the oxygen ions is in the state O^- without receiving an electron, i. e., a cluster $Li^+-(3O^{2-}+O^-)$ is formed. Due to the high electronegativity of oxygen the ion O^- takes one electron from the ion Fe^{2+}, while the first ion is recharged to the normal state O^{2-}, and the second ion — to state Fe^{3+} (d^5-configuration). Clusters $Fe^{3+}-4O^{2-}$ and Li^+-4O^{2-} are formed, they are deformed in different ways: the first is due to the excess charge of the ion Fe^{3+} contracts, and the second one expands due to insufficient charge of the ion Li^+. The ions Fe^{3+} and Li^+ form complexes $Fe^{3+}-Li^+$, called dimers and clearly observed in EPR signals. The number of ions Fe^{3+} and Li^+ is the same, therefore, the number of clusters $Fe^{3+}-4O^{2-}$ and Li^+-4O^{2-} is the same too. Therefore, the above described deformations do not lead to change in the crystal volume. However, due to the formed dimers $Fe^{3+}-Li^+$, which are electric dipoles and are randomly distributed throughout the crystal, a non-uniform electric field occurs.

In 1992 in the photoluminescence (PL) spectra of ZnO a narrow radiative recombination line was detected [4] at an energy of 1.7874 eV, called the A-line. In the case of $\mathbf{E} \parallel \mathbf{C}$ (π-polarization, $\mathbf{C}$ — crystallographic axis of the crystal) A-line was very intense, its width at half maximum was $48\,\mu$eV at temperature $T = 1.8$ K. But in the case of $\mathbf{E} \perp \mathbf{C}$ (σ-polarization) the line was by several times weaker (Figure 2 from the paper [4]). This seemed to be an unusual property. The authors of the paper [4] attributed A-line to transition $^4T_1 \rightarrow {}^6A_1$ between states characteristic of cubic symmetry. It was not considered that in ZnO crystal the cluster $Fe^{3+}-4O^{2-}$ has local symmetry C_{3v}. In this case, the first excited state of d^5configuration ^4G has another splitting. As will be shown further, in this case, the first by energy degenerate excited state arising as a result of such splitting turns out to be of the type ^4E, and not $^4T_1$, as for cubic symmetry.

2. Experimental conditions

In this paper, the PL spectrum of hydrothermal single crystals ZnMnO:Fe^{3+} was recorded on Fluorolog 3 spectrofluorimeter of the HARIBA system, equipped with cryogenic system with the ability to cool the sample temperature to 4.2 K. Measurements were made at temperature of 4.5 K. A built-in xenon lamp was used for excitation, the light of which was passed through a monochromator. The excitation energy was equal to 3 eV, and the spectral width of the monochromator slit was 0.1 nm, which corresponded to 0.285 meV or 2.3 cm^{-1}. PL spectra were recorded using a Rochon prism polarizer [5], through which radiation was passed to determine the polarization of the light exiting the sample, and then the radiation was incident on a photodetector. The light polarization is necessary since the crystal under study is uniaxial. Samples $Zn_{1-x}Mn_xO$ ($x = 0.0009$) for studies were obtained by the hydrothermal synthesis method developed by G.A. Emel'chenko at the Institute of Solid State Physics of the Russian Academy of Sciences (Chernogolovka). The samples had the shape of rectangular parallelepipeds with dimensions $0.6 \times 0.35 \times 0.07\,\text{cm}^3$, cut perpendicular to the optical axis **C**. X-ray diffraction analysis of the samples was carried out on Rigaku XtaLAB diffractometer at room temperature.

3. Results and discussion

Obtained PL spectra with electric vector $\mathbf{E} \perp \mathbf{C}$ (σ-polarization) and $\mathbf{E} \parallel \mathbf{C}$ (π-polarization), **C** — crystallographic axis of the crystal, are presented in Figure 1 in the spectral region 1.650–1.792 eV. The line A is shown zoomed up in Figure 2. In ZnMnO crystals, as can be seen from Figures 1 and 2, the A-line is observed for both polarizations with similar intensities, while the line is asymmetrically broadened. In this case, in comparison with the paper [4] A-line is slightly shifted and is observed at an energy of 1.7899 eV. At the short-wavelength decay of the line in the case of σ-polarization, against the background of asymmetric broadening an additional feature is observed — a weak peak (Figure 2). In the case of π-polarization the line has an asymmetric shape with a feature in the form of a shoulder at the short-wavelength decay. Weak peak at energy 1.7916 eV observed for σ-polarization can be understood as a result of the excited state ^4E splitting. A comparison of the PL spectra of ZnMnO crystals obtained in this paper with similar spectra of ZnO:Fe crystals from the paper [4] shows the following. The line A and all other features (phonon repetitions and local oscillation, separated from the line A by 508.3 cm^{-1}) are reproduced at approximately the same frequencies, as in paper [4], but are significantly wider. For example, the line itself A has width at half maximum of 1.634 meV for σ-polarization and 1.636 meV for π-polarization against 48 μeV for π-polarization in paper [4].

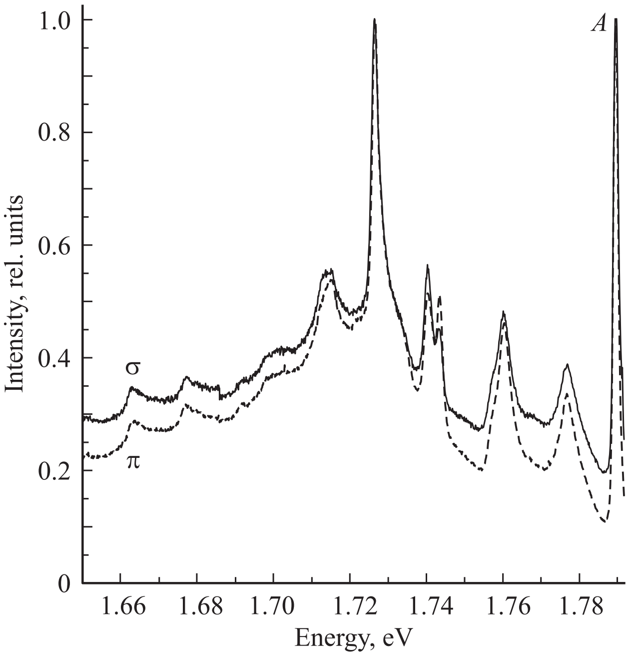

Figure 1. Photoluminescence spectra of ZnMnO:Fe^{3+} single-crystals at $T = 4.5\,\text{K}$ in the region of A-line for σ-polarization (solid curve) and π-polarization (dashed curve). The spectra are normalized to the maximum intensity value of the local vibration peak at energy of 1.723 eV.

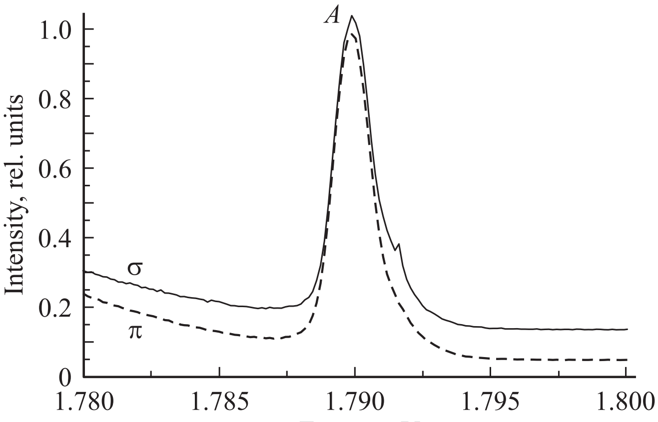

Figure 2. Photoluminescence spectra of ZnMnO:Fe^{3+} single-crystals at $T = 4.5\,\text{K}$ in the region of A-line for σ-polarization (solid curve) and π-polarization (dashed curve). Excitation energy $E_{ex} = 3\,\text{eV}$. The spectra are normalized to the maximum intensity value of the local vibration peak at energy of 1.723 eV.

In the field of C_{3v}-symmetry the splitting of state ^4G has the following view:

$$^4G = 2^4A_1 + {}^4A_2 + 3^4E. \tag{1}$$

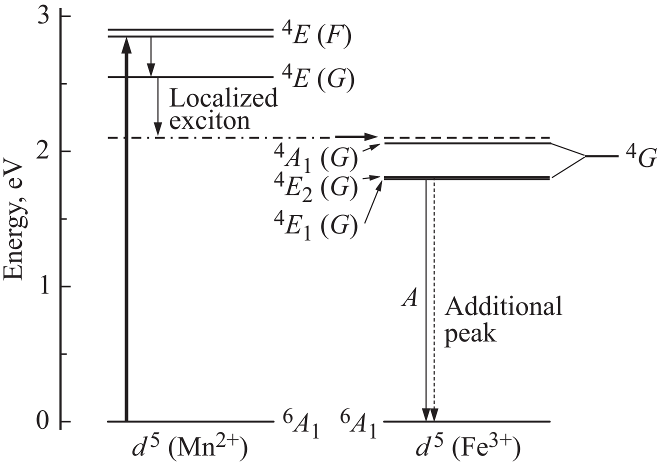

Figure 3. Comparative arrangement of intracenter states of configurations d^5 for ions Mn^{2+} and Fe^{3+}. The dash-dotted line shows the energy of localized exciton. The splitting of the first excited state $4G$ in the symmetry field C_{3v} is also shown.

In this case, two types of doubly degenerate states E arise:

$$3^4E \rightarrow 2E_1 + E_2. \qquad (2)$$

These two types have different kinds of basis functions: $E_1\,(x, y)$, $E_1\,(x^2 - y^2, xy)$, $E_2\,(xz, yz)$. The coordinate system used for symmetry is C_{3v}. The axis z coincides with the crystallographic axis C, passing through impurity manganese ion and one of the oxygen ions; the axis y is directed through the manganese ion perpendicular to the axis z, so as to be in the same plane with the axis z and the second oxygen ion. The axis x is directed at angle of 120° to the axis y, also through the manganese ion perpendicular to the axis z, so as to be in the same plane with the axis z and the third oxygen ion. In this case, if you look against the direction of the axis z, then the rotation from the axis x to the axis y shall be carried out counterclockwise. The first of the basis functions corresponds to p-electrons. Two other functions — $E_1\,(x^2 - y^2, xy)$ and $E_2\,(xz, yz)$ are responsible for d-electrons. Thus, the Jahn-Teller effect arises, and the state E_1 turns out to have lower energy than E_2 [6].

The ZnMnO crystal differs significantly from ZnO in the presence of an intense impurity absorption band. As shown in the paper [7], at energies slightly below the edge of this band, excitons localized on the cluster Mn^{2+}–$4O^{2-}$ can appear. They differ from traditional localized excitons by the interaction of free electron with hole localized on the oxygen ion. It should seem that the Auger relaxation characteristic of the localized exciton shall end with the excitation of Mn^{2+} ion and its subsequent radiative recombination, as is usually occurs. Namely, the exciton localized on impurity center $3d$ or $4f$ annihilates, but due to the Coulomb interaction the electron from the impurity center $3d$ or $4f$ gets excited. The excitation energy is equal to the energy of the localized exciton. The $3d$- or $4f$-ion excited in this way goes into the ground state, emitting a light quantum with energy equal to the excitation energy of the impurity center. But in ZnMnO compound such a process does not occur, since the energy position of the edge of the intense absorption band corresponding to the energy of localized exciton on the cluster Mn^{2+}–$4O^{2-}$ is approximately equal to 2.1 eV, which is significantly below the energy of the first intracenter transition for the configuration d^5 of ion Mn^{2+}, equal to 2.55 eV (the energies of the next transitions are 2.85 and 2.9 eV) [8]. Then the question arises about the energy transfer from localized exciton. Since the crystal contains ions Fe^{3+}, then it can be assumed exactly these ions are excited. In other words, a more complex Auger relaxation process takes place, associated not with one, but with two impurity centers. Figure 3 shows the comparative arrangement of intracenter states of the configurations d^5 for the ions Mn^{2+} and Fe^{3+}. In the case of cubic symmetry, the first excited state $^4T_1$ of the ion Fe^{3+} is separated from the ground state $^6A_1$ by energy of approximately 1.8 eV. We assume that in the case of symmetry C_{3v} the difference in energies between the doublet ^4E and the state $^6A_1$ will be of the same order. Taking into account the Stokes shift in the absorption spectrum, this state shall have an even higher energy. The state $^4A_1$ of the ion Fe^{3+} may be located slightly higher in energy, which, like the doublet ^4E, arises as a result of splitting of the state ^4G in the symmetry field C_{3v} (1) and which, in principle, can be close to the energy of the exciton localized on cluster Mn^{2+} – $4O^{2-}$, as shown in Figure 3. Therefore, we can expect that during annihilation of such exciton due to the Coulomb interaction, one of the electrons d-shell of the ion Fe^{3+} is excited [9]. This process is shown in Figure 3 with a thick horizontal arrow. Thus, the ion Fe^{3+} (d^5) finds itself in one of the excited states and, as a result of nonradiative recombination, enters the first excited state in energy $^4E_1$. Its radiative relaxation to the ground state $^6A_1$, as for ZnO:Fe crystal, appears in the PL spectrum as A-line. Slightly higher in energy than $^4E_1$ is the state E_2, the transition from which to $^6A_1$ causes weak peak on the high-energy decay of A-line. As for the ion Mn^{2+}, then, as already noted, its first excited state has energy of 2.55 eV; it also is a doublet $^4E\ (G)$, resulting from splitting (1) state ^4G in the symmetry field C_{3v}. The following excited states with energies of 2.85 and 2.9 eV are also states of type ^4E, they arise as a result of splitting in the symmetry field C_{3v} of the state ^4F. In Figure 3 these states are marked as $^4E\ (F)$. When samples are irradiated by exciting radiation from a source with energy of 3 eV, the ions Mn^{2+} find themselves in the state $^4E\ (F)$, this excitation process is shown in Figure 3 with thick vertical arrow. Then they relax nonradiatively into the $^4E\ (G)$state, and in the process of further relaxation the exciton of the above type appears, localized on the Mn^{2+}–$4O^{2-}$ cluster. All these processes are also shown in Figure 3. As for ZnO:Fe crystal in paper [4], the line A is accompanied by a large number of phonon repetitions, and at energy of about

1.723 eV an intense peak is observed, corresponding to local vibration. The broadening of the observed lines (especially the line *A* and the peak of the local vibration) in comparison with ZnO : Fe crystal in the paper [4] can be explained as follows. As already noted, ZnMnO crystals under study contain ions Fe^{3+} and Li^{+}, charged relative to the lattice. Due to the distribution of these ions in the crystal, the non-uniform electric field arises. The latter causes the Stark effect, which affects the energy states of the ions. The broadening of the lines occurs of the exciton localized on the $\mathrm{Mn}^{2+}-4\mathrm{O}^{2-}$ cluster, which is also transferred to Fe^{3+} ions, the excitation of which is caused by the annihilation of this exciton. This effect can explain the line broadening observed in the PL spectrum of ZnMnO. According to the paper [10], the theoretical description of the configuration d^5 is itself a very difficult task. The description of the Auger process that takes place in our case seems to be much more complicated, since it is associated with two impurity centers of the configuration d^5, between which interaction is possible.

4. Conclusion

Finally, we note the following main results obtained in our paper. Firstly, in ZnMnO : Fe^{3+} crystals there is a line *A* that arises as a result of radiative recombination $^4E_1-{}^6A_1$ of Fe^{3+} ion (configuration d^5). Fe^{3+} ion transition to the excited state $^4E_1$ is caused by the Auger process associated with two impurity centers Mn^{2+} and Fe^{3+}. At the short-wavelength edge of the line *A* an additional feature appears in the form of weak peak in the case of $\mathbf{E} \perp \mathbf{C}$ and a shoulder in the case of $\mathbf{E} \parallel \mathbf{C}$. This feature can be understood as the splitting of the excited state ^4E of the iron ion Fe^{3+}, resulting from the Jahn-Teller effect. Secondly, in ZnMnO : Fe^{3+} crystals, compared to ZnO : Fe^{3+} the line *A* is by several times larger in width due to the Stark effect. Thirdly, in ZnMnO : Fe^{3+} crystals the line *A* has approximately the same intensity for both polarizations, while for ZnO : Fe^{3+} it has greater intensity only in the case of $\mathbf{E} \parallel \mathbf{C}$, and for $\mathbf{E} \perp \mathbf{C}$ it is by several times weaker.

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Conflict of interest

The authors declare that they have no conflict of interest.

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