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The manifestation of local vibrations in photoluminescence spectra of ZnO : Fe^{3+}

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In this paper photoluminescense spectra and EPR-signals of ZnO single crystals, doped with manganese and containing (from EPR data) uncontrolled impurity of iron, were investigated. At the temperature of 4.5 K in photoluminescense spectrum the band in energy interval of 1.55–1.8 eV ($12493-14508\,cm^{-1}$) was observed. This band contains some intensive lines; these lines are caused by Fe^{3+} ions (d^5-configuration). The first and most intensive line at the energy of 1.79 eV corresponds to irradiative transition $^4T_1 \rightarrow {}^6A_1$ in Fe^{3+} ions. The other peaks are electronic-vibrational structure. This structure may be caused by force interaction in deformed Fe^{3+}-$4O^{2-}$ cluster.

Keywords: zinc oxide, Fe^{3+} impurity, photoluminescence, EPR.

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Introduction

A detailed study of the optical absorption of hydrothermal Zno : Mn single-crystals was carried out in the papers [1,2]. In the EPR spectra of these crystals, along with signals from Mn^{2+} ions, signals belonging to an uncontrolled impurity of Fe^{3+} ions (d^5configurations) were detected. The signals of Fe ions $^{3+}$ were approximately two orders of magnitude weaker than the signals corresponding to ions Mn^{2+}. They were significantly weakened when the crystal was illuminated with a xenon lamp, while the signals of Mn^{2+} ions did not respond to illumination. Fe^{3+} ion lines were observed in photoluminescence (PL) spectra in papers [3,4]. The authors of [3] have shown that in the PL spectrum of ZnO crystals, when excited by a two-watt Ar^+ ion laser at a temperature of 1.8 K, there is a A line at an energy of 1.78742 eV ($14406.6\,cm^{-1}$), which was interpreted as the intracenter transition $^4T_1 \rightarrow {}^6A_1$ of the $Fe^{3+}(d^5)$ ion. This line was accompanied by a large number of vibrational repetitions in energy interval of 1.66084–1.77468 eV (13386.37 $-14303.92\,cm^{-1}$). One of the replicas at the energy of 1.72417 eV ($13896.81\,cm^{-1}$) was as intense and narrow as the zero-phonon line A. All the lines were identified as phonon replicas.

In the paper [4] PL spectrum was observed in the interval of $13250-14500\,cm^{-1}$ on single-crystal samples obtained by the hydrothermal method and the chemical gas transport method. The observed spectrum [4] was interpreted by the authors of [5] by analogy with the paper [3], assuming that all vibrational replicas of the zero-phonon line are due to interaction with lattice phonons.

The aim of this paper is to reveal the contribution of the Fe^{3+}–$4O^{2-}$ cluster states to the luminescence spectrum of manganese-doped ZnO samples. The radius $3d^5$-configuration of the Fe^{3+} ion, according to [6], noticeably differs from the radius of the Zn^{2+} ion — by 0.11 Å. In addition, the Fe^{3+} ion has a positive charge relative to the lattice. This should result in significant changes in the force interaction in the $Fe^{3+}-4O^{2-}$ cluster and the formation of local oscillations.

Experiment description

In this paper, ZnO : Mn samples obtained by the hydrothermal method at the ISSP of RAS (Chernogolovka) were studied. Intentional doping of the samples with iron was not carried out, but the iron impurity was present in these samples as uncontrolled. It was found by observing the EPR signals corresponding to this impurity. The crystal grown was carried out during a month in a liquid medium containing lithium compounds. That is why there are also Li^+ ions in the crystal. They are negatively charged in relation to the lattice, since, unlike the substituted zinc ion, they donate one electron, not two. To compensate for this charge, the residual iron Fe^{2+} (d^6) ions donate one electron and end up in the state Fe^{3+} (d^5). EPR signals were recorded on an EMX Plus Bruker spectrometer at

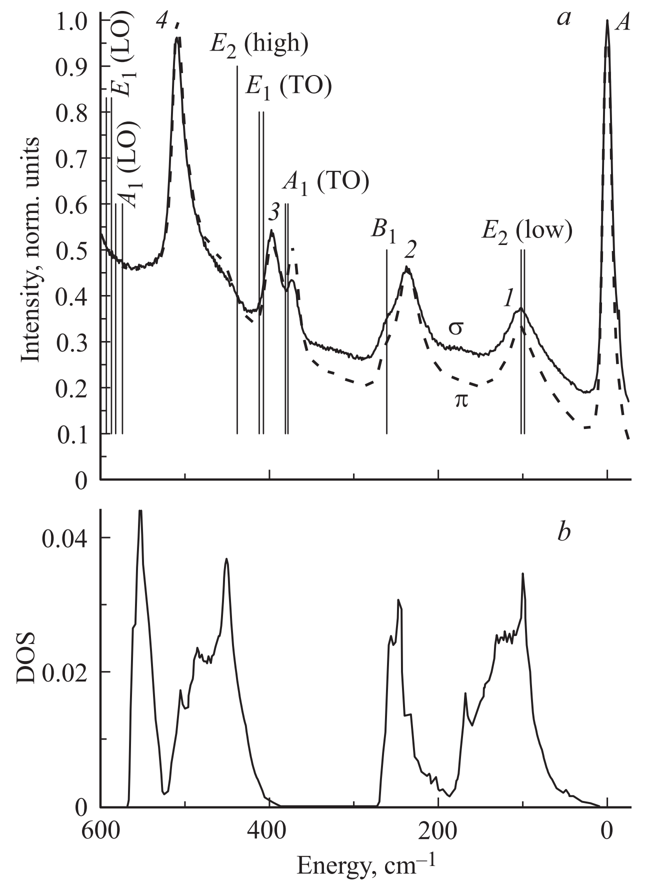

Figure 1. (*a*) PL spectra of ZnO:Mn, Fe single-crystals at $T = 4.5$ K for σ- (solid curve) and π polarization (dashed curve). Comparison of the energies of vibrational satellites of the zero-phonon line *A* with the energies of natural oscillations A_1, B_1, E_1 and E_2 of ions of the zinc oxide base unit, consisting of two zinc ions and two oxygen ions. The vertical lines show the self oscillation energies A_1, E_1 and E_2 (low) observed from the Raman light scattering of ZnO. (*b*) Phonon density of states.

temperatures of 300 and 120 K at frequencies of 9,852 and 9,450 MH, respectively, with the direction of the magnetic field induction vector both parallel and perpendicular to the optical axis **C** of the samples. The PL spectra in the area of the *A* line and its vibrational replicas were recorded on a Fluorolog3 spectrofluorometer (Horiba) equipped with a cryogenic system capable of cooling to a temperature of 4.2 K. A built-in xenon lamp was used for excitation, the light of which was passed through a monochromator. The spectral resolution was 0.5 cm^{-1}. The PL spectra were recorded using a Rochon prism polarizer, through which radiation was passed to polarize the light emerging from the sample, and then the radiation was incident on a photodetector. Polarized light should be used because the crystal under study is uniaxial. Light can be polarized: either the electric vector of the light wave **E** is parallel to the crystallographic axis **C** of the sample ($\mathbf{E} \parallel \mathbf{C}$, π-polarization), or perpendicular ($\mathbf{E} \perp \mathbf{C}$, σ-polarization).

Findings and discussion

Fig. 1, *a* shows the PL spectra of a ZnO:Mn sample with a residual Fe impurity at a temperature $T = 4.5$ K in the interval of $12660-14700$ cm^{-1} for σ- and π-polarizations of radiation. Meanwhile, the position of the zero-phonon line *A* (14426.43 cm^{-1}) is taken as zero, then the modulus of the difference between the energy positions of the corresponding replicas and the zero-phonon line itself is plotted along the energy axis. For both polarizations, the spectra consist of a zero-phonon line *A* and a series of vibrational repetitions of this line. The *A* line is due to the intracenter transition $^4T_1 \rightarrow {}^6A_1$ of the Fe$^{3+}(d^5)$ ion, as was shown in [3]. The impurity of manganese does not change the positions of the lines, but the lines themselves look broadened in comparison with the data of the paper [3]. Apparently, the broadening arises precisely due to manganese ions. The structure of the vibrational repetitions for both polarizations is very similar, only for the doublet satellite *3*, with σ polarization, the low-energy component has a much higher intensity than the high-energy one, while in case of π polarization, the intensities of both components are approximately the same. These spectra differ significantly from the PL spectra of the II$-$VI:Mn compounds, where, as a rule, there is a fairly wide band with a sharp rise and a smooth decay, due to the intracenter transition $T_1 \rightarrow {}^6A_1$. The broad bands of the intracenter PL are due to transitions with a change in the ratio of the numbers of t_2- and *e* electrons of the 3*d* shell of the d^5 configuration, for example, $2t_2 + 3e \rightarrow 3t_2 + 2e$. This is the transition $^4T_1 \rightarrow^6 A_1$, and therefore it is accompanied by many emitted phonons [7]. It can be noted that, in our case, intense vibrational repetitions have a background component characteristic for the PL of II$-$VI:Mn compounds.

Oscillations of the ZnO lattice are characterized by the movement of ions of a primitive cell consisting of two Zn^{2+} ions and two O^{2-} ions. These oscillations are called eigenmodes and occur either along the **C** crystallographic axis or perpendicular to this axe. They are classified as A_1(TO), A_1(LO), B_1, E_1(TO), E_1(LO), E_2 (low), E_2(high) [8,9]. Intense vibrational repetitions are due to the specifics of the Fe^{3+} (d^5 ions) and its nearest environment. Fig. 1, *a* also shows a comparison of the energies of the vibrational repetitions with the energies of the characteristic oscillations A_1, B_1, E_1, E_2. It is clearly seen that the frequency of the phonon replica *4* does not coincide with the frequencies of the eigenmodes.

Fig. 1 shows a comparison of the PL spectra of ZnO:Mn with an uncontrolled Fe impurity with the density of states of phonons of the zinc oxide lattice according to the data of [10]; the latter is shown at the bottom of Fig. 1, *b*. It can be seen that the *1* and *2* satellites approximately correspond to the maxima of the density of states. The maxima of the satellites *3* are located at the very beginning of one of the branches of the density of states, and the most intense satellite *4* falls into a dip between two branches of the density of phonon states of the lattice, where this density is

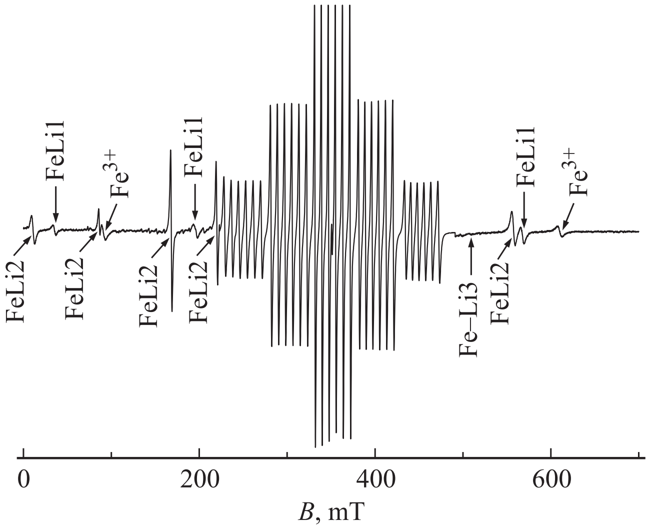

Figure 2. EPR spectrum of a ZnO : Mn,Fe sample at a frequency of 9852 MHz. The measurement temperature is 300 K, the magnetic field is directed parallel to the crystallographic axis of the sample (**B** ∥ **C**). The intensity of five electronic transitions Mn^{2+} with hyperfine structure sextets in the range of fields 223−491 mT is reduced by 10 times. The arrows indicate signals from single Fe^{3+} ions and three types of Fe^{3+}−Li^{+} dimers.

nonzero, but very small. This allows to consider the *3* and *4* peaks as quasi-local oscillations arising in the deformed part of the lattice. More detailed studies are necessary to finally elucidate the nature of these peaks. The local deformation of the lattice is caused by the impurity Fe^{3+} ion, which replaces Zn^{2+}, due to the excess charge. The lattice deformation near the Fe^{3+} ion consists of displacements of four O^{2-} ions and twelve Zn^{2+}ions. Such a complex deformation is difficult to analyze. Therefore, for the sake of simplicity, we will consider only the oscillative states of the Fe^{3+}-4O^{2-} cluster, which has the symmetry C_{3v}, i.e. the central ion and the first coordination sphere. In this cluster, various fully symmetrical oscillations can occur: O^{2-} ion along the **C** axis relative to the center of the cluster, three O^{2-} ions toward the center of the cluster, and Fe^{3+} ion along the **C** axis. It can reasonably be assumed that the oscillation frequency of the O^{2-} ion will be the highest, the oscillation frequency of the three O^{2-} ions will be lowered, and the oscillation frequency of the Fe^{3+} ion will be the lowest. Thus, it can be thought that the local oscillation *4* (Fig. 1) is the oscillation of the O^{2-} ion along the optical axis **C** [3,5]. The *2* and *1* peaks (Fig. 1), which approximately coincide in position with the peaks in the density of phonon states, are due to oscillations of three O^{2-} ions and Fe^{3+} ion, respectively.

In order to understand the structure of the Fe^{3+} centers responsible for the observed PL, signals from the EPR spectrum of ZnO:Mn samples with an uncontrolled Fe impurity were recorded. We present the EPR spectra in order to show that the iron impurity in our crystals actually manifests itself, and in order to judge the low concentration of the iron impurity as well as. Fig. 2 shows strong signals of Mn^{2+} ions and weak signals of d^5-configuration of Fe^{3+} ions. The intensity ratio of the Mn^{2+} and Fe^{3+} signals indicates that the concentration of the residual iron impurity is very low. The intense signals of manganese ions were discussed in [1,2]. Along with the signals due to isolated Fe^{3+} ions, there are also signals of Fe^{3+}-Li^{+} dimers (also weak), and several variants of dimers appear, which is associated with different relative positions of iron and lithium ions.

The presence of lithium impurities in the crystal is due to the peculiarities of the hydrothermal growth method [12]. The structure of the EPR signals for Fe^{3+}-Li^{+} agrees with those previously observed and discussed in papers [4,5,11–13]. The most reliable identification of the nature of dimers was obtained in [13] using electron-nuclear double resonance spectroscopy. Despite the presence of a large number of Mn^{2+} centers in the crystal, the spectra of isolated Fe^{3+} ions and Fe^{3+}-Li^{+} dimers observed by us are in good agreement with the results of [5,11–13].

Conclusion

The study of the EPR signals of Fe^{3+} ions in ZnO over a long period of time [4,5,11–13] resulted in an understanding of the difference in the structure of isolated Fe^{3+} centers and Fe^{3+}-Li^{+} dimers. Oscillative satellites in the intracenter PL spectrum of Fe^{3+} ions in ZnO were observed for the first time in 1992 [3]. In the PL spectrum of ZnO:Mn,Fe^{3+} (d^5), a narrow line of the $^4T_1 \to {}^6A_1$ intracenter transition and an extensive series of its vibrational repetitions were found. All vibrational repetitions, except for one, were understood as the emission of lattice phonons in the process of intracenter emission transitions. Meanwhile, the structure of the spectrum differs significantly from the intracenter transitions observed for compounds II −VI:Mn^{2+}. We believe that the narrow line of the $^4T_1 \to {}^6A_1$ intracenter emission transition in ZnO:Fe^{3+} (d^5) is accompanied by local oscillations of the deformed Fe^{3+}-4O^{2-} cluster. The vibrational repetitions *1* and *2* (Fig. 1), as a comparison with the density of states shows, can be associated with lattice phonons, and the peaks *3* and *4*, noticeably shifted in their position relative to the phonon density peaks, can be considered with high confidence as quasi-local oscillations. Additional studies are necessary to finally elucidate the nature of these peaks. For comparison, the authors of the papers [4,5] consider only the peak *4* to be a local oscillation, while the rest are attributed to phonons. The large width of the vibrational repetition peaks can be explained by the existence of different types of Fe^{3+} [5,11,12,13] centers and, consequently, by the presence of a spectrum of close local oscillations. In the spectra obtained, the zero-phonon line *A* and its vibrational repetitions are observed at the same energies as in the paper [3], but are significantly broadened. In our opinion, the reason for this broadening is the impurity of manganese. So far, there is no clear understanding of the structure of local oscillations (namely, there is no understanding of the frequency of the peaks, their much greater width compared to the line of the intracenter transition $^4T_1 \to {}^6A_1$).

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Conflict of interest

The authors declare that they have no conflict of interest.

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