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ODMR study of ZnO single crystals containing iron impurity ions

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Abstract. Optically detected magnetic resonance (ODMR) was studied in ZnO single crystals containing iron impurity ions. ODMR spectra of the ground state of isolated Fe^{3+} on the Zn^{2+} lattice sites were obtained by monitoring the intensity of the intra-centre Fe^{3+} luminescence together with the ODMR signals of shallow donors. The latter observation suggests that the Fe^{3+} luminescence may actually be excited due to energy transfer from the recombining donor-acceptor pairs to the impurity ions. This conclusion is supported by the presence of Fe^{3+} emission in the afterglow spectra recorded after switching off band-to band excitation light.

1. Experimental

ZnO is a very promising material for semiconductor device applications [1]. It has a direct and wide band gap in the near-UV spectral region and a large free-exciton binding energy so that exciton emission processes can persist at or even above room temperature. The availability of large single crystals is a big advantage of ZnO over GaN and allows using ZnO single crystals as substrates for MBE grown layers and nanostructures. The epitaxy of ZnO films on native substrates can result in ZnO layers with reduced concentration of extended defects and, consequently, better performance in electronic and photonic devices.

The inevitable presence of transition metals even in high-quality II-VI semiconductors is well known. A quite-common accidental contamination forming deep traps is Fe. On the other hand ZnO:Fe is considered as the interesting candidate for quantum computing applications.

The most successful experimental technique for identifying and studying the defects has often proven to be electron paramagnetic resonance (EPR) [2]. Optically detected magnetic resonance (ODMR) [3, 4] provides a huge increase in sensitivity (up to a single quantum object [5]) and can be applied for a study of spin-dependent recombination and energy transfer processes. EPR and luminescence of transition metal ions in ZnO were widely studied [6, 7] but, to our knowledge, no ODMR results were reported so far with the exception of ref. [8], where ODMR of V^{2+} was observed.

In the present paper, we report preliminary results of a study using optical detection of electron paramagnetic resonance in the photoluminescence of ZnO single crystals containing iron impurity ions.

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2. Experimental

The samples were cut from M-plane ZnO substrates grown by hydrothermal method. Such substrates are used for MBE growth of non-polar ZnO layers and nanostructures. Photoluminescence (PL) was excited with a deuterium arc lamp with appropriate glass filters or a 405 nm semiconductor laser and detected with a grating monochromator and a PM tube. EPR was studied with a commercial X-band spectrometer. The 35 GHz ODMR spectra were recorded at 1.8 K via PL intensity either using on-off modulation of microwaves and lock-in amplification or without modulation. The samples were placed in the centre of a cylindrical H_{011} microwave cavity which had holes for excitation and emission light. The sample could be rotated about vertical axis, which allowed studying angular dependences of the spectra.

3. Results and discussion

The PL spectra of ZnO crystals under 405 nm excitation are shown in figure 1(a). The upper spectrum was recorded with low spectral resolution, which was used in most of the ODMR experiments. The high resolution luminescence spectrum is shown below. One can see that in addition to the broad band with a maximum around 600 nm, a richly structured luminescence in the spectral range of 680-800 nm is observed. In Ref. [9] this structured spectrum was unambiguously assigned to the $^4T_1(G)$- $^6A_1(S)$ transition of isolated Fe^{3+} ions on Zn^{2+} lattice sites by means of emission, excitation, and magneto-optical spectroscopy. The EPR characterization of the samples confirmed the presence of Fe^{3+} impurity ions in the sample along with traces of Mn^{2+} and Co^{2+} in lower concentration.

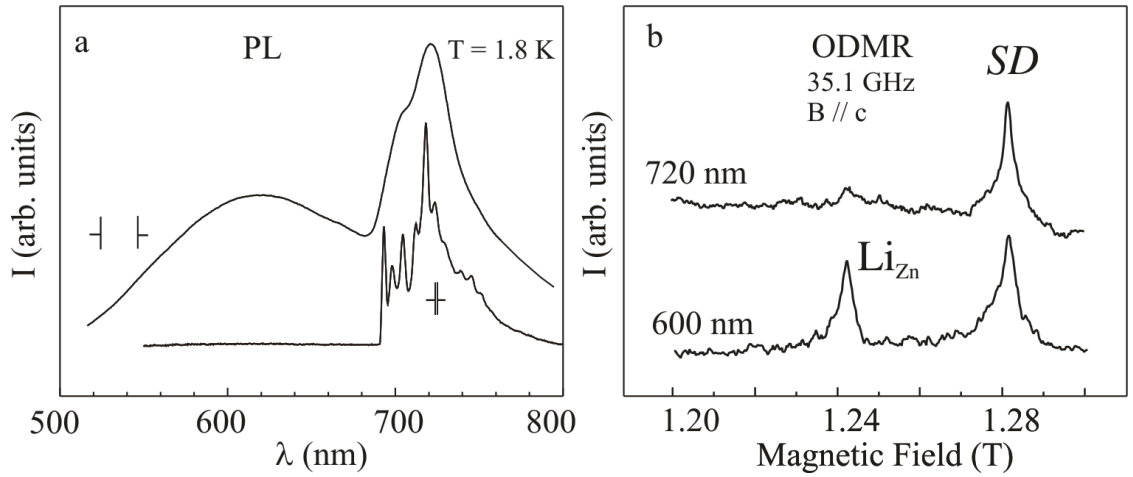

Figure 1. (a) Photoluminescence spectra recorded at 1.8 K in ZnO crystal with high spectral resolution (lower curve) and low spectral resolution used to study ODMR (upper curve). (b) Q-band ODMR spectra recorded via PL intensity without modulation of microwaves at 600 nm (lower curve) and 720 nm (upper curve). B // c.

In the ODMR spectra recorded via the intensity of the broad PL band around 620 nm the well known ODMR spectrum of shallow donors (*SD*) with *g*-factor about 1.96 [10] and lithium acceptors Li_{Zn} [11] were observed. The spectral dependence of both donor and acceptor ODMR signals obtained with microwave modulation at audio frequency and lock-in amplification is close to the broad PL band, which proves that in our samples PL in this range is dominated by the recombination *SD*-Li_{Zn}.

Figure 1(b) presents the ODMR spectra recorded on the PL intensity at 600 nm and 720 nm with cw microwaves applied. It is important that the shallow donor ODMR signal was detected not only within the D-A recombination band but within the iron intra-centre emission too. In contrast to the recombination band no ODMR signals could be seen via the Fe^{3+} emission with modulation of microwaves. The spectral dependence of the shallow donor ODMR in the spectral range of Fe^{3+}

emission is shown in figure 2. One can see that the ODMR amplitude follows very precisely the PL spectrum corresponding to $^4T_1(G)$ - $^6A_1(S)$ transitions of Fe^{3+}.

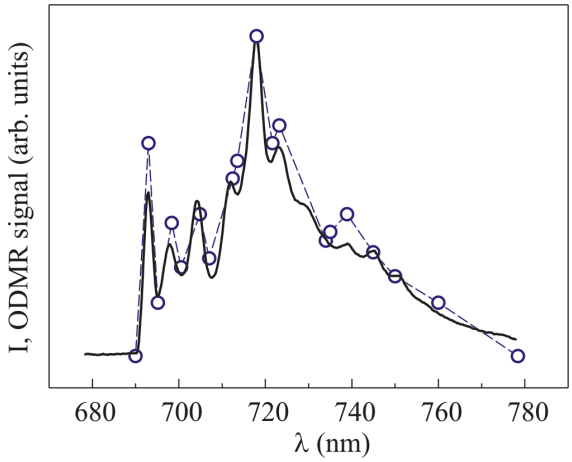

Figure 2. Spectral dependence of the shallow donor ODMR amplitude (open circles) and the PL spectrum of Fe^{3+} under 405 nm excitation (solid line) recorded with the same spectral resolution as was used for ODMR. Dashed line is a guide for eye.

Observation of the shallow donor ODMR on the iron intra-centre PL implies that the Fe^{3+} luminescence may actually be excited due to energy transfer from the recombining donor-acceptor pairs to the impurity ions.

Strongly anisotropic ODMR lines were found in the ODMR spectra recorded via the Fe^{3+} emission intensity in addition to the shallow donor (*SD*) line. Figure 3 (a) presents the ODMR spectrum for $\theta = 55^o$, where θ is the angle between the magnetic field and the *c* axis. The positions of the anisotropic ODMR signals for different θ are displayed in Fig. 3 (b) (open symbols) together with the calculated angular dependence for isolated Fe^{3+} ions in ZnO. Calculations have been made with a computational package EasySpin [12]. We used a conventional axial spin Hamiltonian for axial Fe^{3+} [2] with the parameters of Fe^{3+} ions on Zn^{2+} lattice sites in ZnO taken from Ref. [13]. It is to be noted

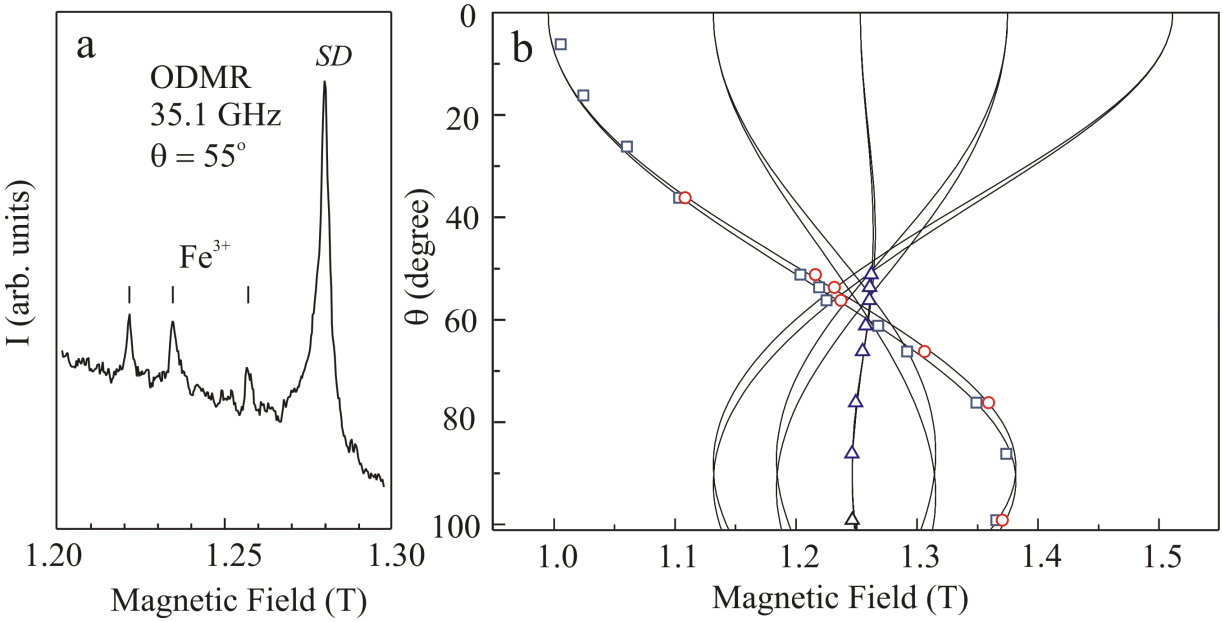

Figure 3. (a) ODMR spectrum recorded in ZnO single crystal via the 720 nm luminescence intensity at 35.1 GHz, T = 1.8 K, $\theta = 55^o$ without modulation of microwaves. (b) Angular dependence of the Fe^{3+} ODMR spectrum. The open symbols are the measured ODMR positions. The lines give the calculated angular dependence using previously established parameters of EPR spectra of the axial Fe^{3+} centres.

that the fine structure splitting parameter is negative: $D = -593.7 \cdot 10^{-4}$ cm^{-1}. The calculated angular dependence is typical for axial $S=5/2$ paramagnetic centres. Small additional doubling of fine structure lines is due to the fact that there are two magnetically distinguishable sites in ZnO lattice for Fe^{3+} on the Zn position with slightly different interactions with the crystal field for certain orientations [13]. A very good agreement between the experimental data and the results of calculations proves that we really detect EPR in the ground state of isolated Fe^{3+} ions via the intensity the intra-centre luminescence of iron.

It should be pointed out that not all fine structure transitions of Fe^{3+} could be observed. For $\theta < 40^{o}$ we have detected only one of five possible fine structure lines that corresponds to the transition between the lowest magnetic sublevels $M_S = -5/2 \leftrightarrow M_S = -3/2$. This seems to be due to the high Boltzmann factor corresponding to EPR conditions, which leads to preferential population of the lowest levels and different intensities of different fine structure EPR lines. Similar behaviour of the fine structure components was reported for high frequency EPR of Mn^{2+} in ZnO crystals and ODMR of Mn^{2+} in CdMnSe quantum dots [14].

A major excitation mechanism of the Fe^{3+} luminescence is generally believed to be the capture of free holes by Fe^{2+} centres [9, 15]. Observation of the shallow donor ODMR via the Fe^{3+} emission in our experiments suggests an energy transfer from the recombining D-A pairs to the impurity ions.

In the samples under study a rather intense afterglow emission could be detected for up to an hour after switching off the UV light excitation. The afterglow spectrum is a wide orange band similar to that reported in [16]. ODMR of lithium acceptors and shallow donors was recorded by monitoring the afterglow intensity, which has unambiguously proved that the afterglow results from the spin-dependent recombination of these centres. In the samples with higher concentration of iron the Fe^{3+} emission was found in the afterglow spectra, which directly confirms the conclusion about energy transfer from the recombining centres to iron impurity ions.

4. Conclusions

ODMR was studied in ZnO single crystals grown by hydrothermal method and containing iron impurity ions. The broad orange band originating from the recombination of shallow donors and Li_{Zn} acceptors was observed in the luminescence spectrum together with a well structured intra-centre luminescence of Fe^{3+} corresponding to $^4T_1(G) - {}^6A_1(S)$ transitions. Anisotropic ODMR signals were found by monitoring the intensity of the Fe^{3+} luminescence. They were unambiguously ascribed to the ground state of isolated Fe^{3+} on Zn^{2+} lattice sites. In addition, ODMR of shallow donors was observed via the intensity of Fe^{3+} intra-centre emission. This suggests that the Fe^{3+} luminescence is excited due to energy transfer from the recombining donor-acceptor pairs to the impurity ions. Observation of the Fe^{3+} emission in the afterglow spectra, which were detected at liquid helium temperatures after switching off excitation light, supports this conclusion.

Acknowledgments

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References

[1] Özgür Ü, Alivov Ya I, Liu C, Teke A, Reshchikov M A, Doğan S, Avrutin V, Cho S-J, and Morkoç H 2005 *Appl. Phys. Reviews* **98** 041301
[2] Abragam A and Bleaney B 1970 *Electron Paramagnetic Resonance of Transition Ions* (Oxford University Press, Oxford)

[3] Cavenett B C 1981 *Adv. Phys.* **30** 475
[4] Baranov P G , Romanov N G 2001 *Appl. Magn. Resonance.* **21** 165
[5] Gruber A, Dräbenstedt A, Tietz C, Fleury L, Wrachtrup J, von Borczyskowski C 1997 *Science* **276** 2012
[6] Mc Cluskey M D, Jokela S J 2009 *J. Appl. Phys.* **106** 071101
[7] Azamat D V, Debus J, Yakovlev D R, Ivanov V Yu, Godlewski M, Fanciulli M, Bayer M 2010 *Phys. Status Solidi* B **247** 1517
[8] Vlasenko L S, Watkins G D, Helbig R 2005 *Phys. Rev*. B **71**, 115205
[9] Heitz R, Hoffmann A and Broser I 1992 *Phys. Rev.* B **45** 8977
[10] Cox R T, Block D, He A, Picard R, Santier C 1978 *Solid State Communs* **25** 77
[11] Schirmer O F 1968 *J. Phys. Chem. Solids* **29** 1407
[12] Stoll S and Schweiger A 2006 *J. Magn. Reson.* **178**, 42
[13] Walsch W M Jr and Rupp L W Jr 1962 *Phys. Rev.* **126** 952
[14] Baranov P G, Romanov N G, Tolmachev D O, Babunts R A, Namozov B R, Kusrayev Yu G, Sedova I V, Sorokin S V, Ivanov S V 2008 *JETP Lett.* **88** 631
[15] Malguth E, Hoffmann A, Gehlhoff W, Gelhausen O, Phillips M R, Xu X 2006 *Phys. Rev.* B **74** 165202
[16] Zwingel D 1972 *J. Lumin.* **5** 385