

## Mn- and Fe- doped GaN for spintronic applications

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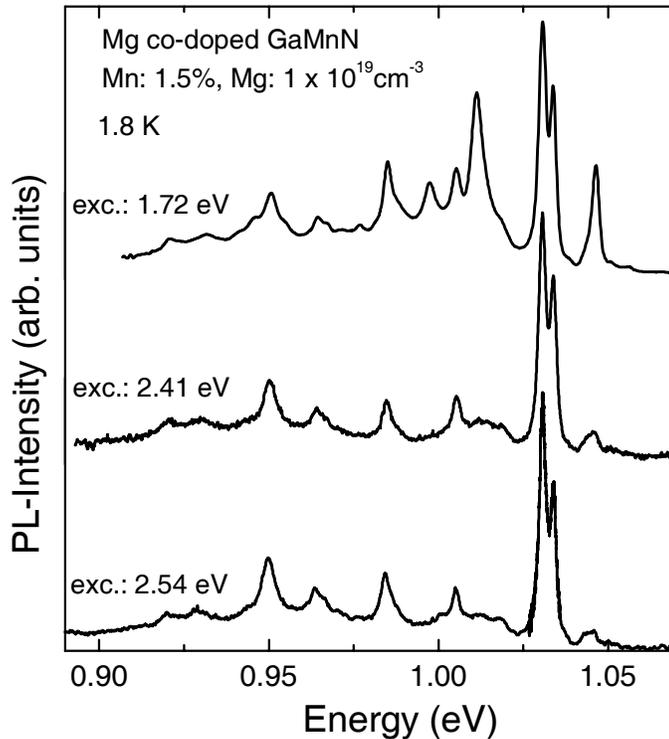
### ABSTRACT

In the context of ferromagnetic spin-coupling in dilute magnetic semiconductors, we present optical investigations on Mg co-doped GaMnN and Fe doped GaN. A complex luminescence feature occurring in Mg co-doped GaMnN around 1 eV was previously attributed to the internal  ${}^4T_2(F) \rightarrow {}^4T_1(F)$  transition of  $Mn^{4+}$  involved in different complexes. Selective excitation studies indicate the presence of at least three different complexes. Photoluminescence excitation spectra suggest that the internal  $Mn^{3+}$  transition may represent an excitation mechanism. Magneto photoluminescence spectra indicate equal  $g$  values for the ground and excited state. Low temperature infrared absorption spectra of Fe doped GaN allow to unambiguously establish the electronic structure of the  $Fe^{2+}$  center in GaN. Our results suggest that the  $Fe^{2+}({}^5T_2)$  state is stabilized against Jahn-Teller coupling by the reduced site-symmetry of the hexagonal lattice.

### INTRODUCTION

Recent studies predict a high potential of a ferromagnetic spin-coupling at room temperature for GaMnN with a high concentration of free holes [1, 2, 3]. In accordingly prepared Mg doped GaMnN material, a rich luminescence structure was detected around 1 eV and attributed to the internal spin allowed  $Mn^{4+}({}^4T_2(F) \rightarrow {}^4T_1(F))$  transition [4, 5]. This interpretation is supported by theoretical considerations suggesting that the  $Mn^{3+/4+}$  donor level is found within the band gap of GaN [6]. As a consequence, Mn incorporation should compensate p-type doping in GaN rendering hole mediated spin-coupling rather difficult to achieve in GaMnN. Until now, no unambiguous evidence could be given that the luminescence feature around 1 eV actually originates from  $Mn^{4+}$ .

Also bound states consisting of a hole bound to an ionized TM center ( $A^-$ ) may play an important role for ferromagnetic spin-coupling [8]. Such a state has been observed in GaN involving  $Fe^{2+}$  [9, 10]. For a good understanding of this effective-mass-like state the electronic structure of the involved  $Fe^{2+}$  center needs to be known. In this work, we present infrared absorption spectra recorded at liquid helium temperatures. These results confirm the electronic structure of the  $Fe^{2+}$  center in GaN that had been established on the basis of measurements at 40 K [11]. These results allow conclusions about the axial distortion of the tetrahedral crystal field in the hexagonal crystal as well as about the Jahn-Teller coupling affecting the Fe center.



**Figure 1.** PL spectra of Mg doped GaMnN excited at different energies. The luminescence lines are attributed to the internal  $\text{Mn}^{4+}({}^4\text{T}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F}))$  transition. Several ZPL's exhibiting different excitation behavior originate from different complexes involving  $\text{Mn}^{4+}$ .

## EXPERIMENTAL

Undoped and Mg co-doped GaMnN films were grown by metal-organic vapor deposition (MOCVD) on sapphire (0001) substrates with GaN templates [12]. They contain 1.5 % Mn and  $1 \cdot 10^{19} \text{ cm}^{-3}$  Mg if co-doped, as determined by secondary ion mass spectroscopy (SIMS). The Fe doped GaN sample was grown by hydride vapor phase epitaxy (HVPE). SIMS investigations yield an Fe concentration of  $1 \cdot 10^{18} \text{ cm}^{-3}$ . For experiments at low temperatures, the samples were immersed in liquid helium. Photoluminescence (PL) was excited using the 488 and 514 nm lines of an Ar-ion laser and a pulsed Ti:sapphire laser tuned to 721 nm. The emitted light was dispersed by a 1-m Spex monochromator and detected by a nitrogen-cooled photomultiplier with a Ge cathode. Fourier transform infra red (FTIR) absorption studies were carried out using the IFS 66v spectrometer from Bruker. In photoluminescence excitation (PLE) experiments a halogen lamp in combination with a 275-mm double monochromator served as tunable light source and a 300-mm double monochromator was used in detection. Zeeman studies were carried out using a 5-T superconducting magnet built in split-coil geometry.

## RESULTS AND DISCUSSION

Figure 1 displays the luminescence structure found in Mg co-doped GaMnN and that was attributed by Han et al. to the internal  $\text{Mn}^{4+}({}^4\text{T}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F}))$  transition in different complexes

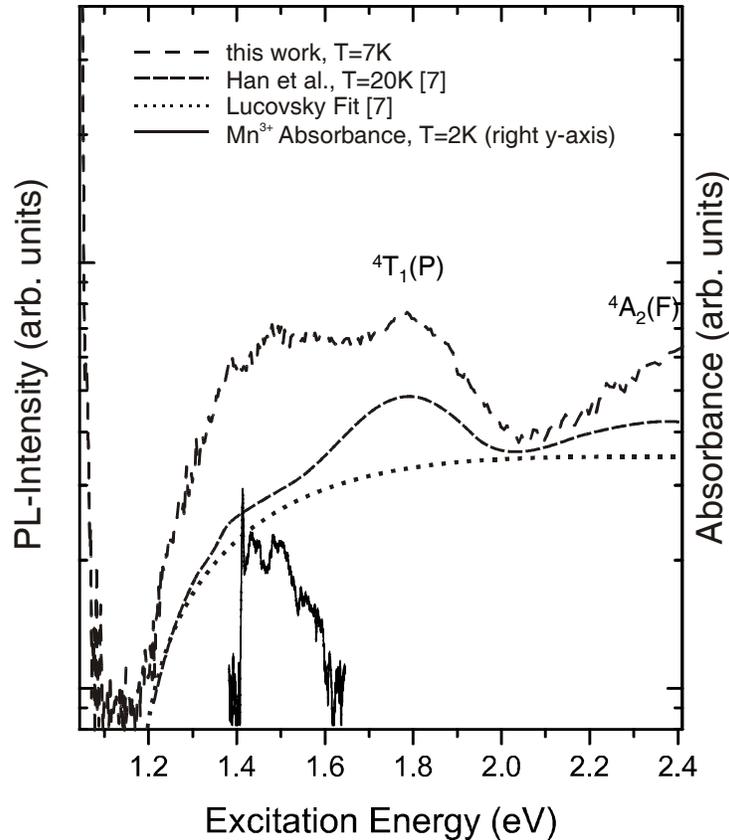
involving  $\text{Mn}^{4+}$  [5]. This attribution is supported by the fact that our Mg co-doped samples do not show a trace of the  $\text{Mn}^{3+}({}^5\text{T}_2 \rightarrow {}^5\text{E})$  transition in transmission spectra [12, 14]. GaMnN samples grown under the very same conditions with the same Mn concentration but without Mg co-doping did show the  $\text{Mn}^{3+}$  transition and not the alleged  $\text{Mn}^{4+}$  transition. Hence, the appearance of these different charge states can consistently be explained by a shift of the Fermi level. Since our transmission experiments suggest that none of the manganese is in the 3+ charge state, we can conclude that in our samples the Fermi level is actually below the  $\text{Mn}^{3+/4+}$  level and not pinned to it. Thus, the Mn incorporation did not completely compensate the p-type doping.

PL lifetimes of around 70  $\mu\text{s}$  support the interpretation as spin allowed transitions with medium oscillator strengths [5]. However, transmission spectra of our Mg doped GaMnN samples do not show any features in the spectral region displayed in Fig. 1. Maybe the observed process is not the  $\text{Mn}^{4+}({}^4\text{T}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F}))$  transition but a forbidden one with low oscillator strength. In this case, the lifetimes could be shortened by non-radiative processes.

The spectra in Fig. 1 were excited at three different laser energies 1.72 eV, 2.41 eV and 2.54 eV. In combination with the spectra recorded at excitation energies of 1.27 eV and 3.81 eV by Han et al., we can now get a rough image of the respective excitation behavior of the different luminescence lines. At high below band gap excitation energies (e.g., 2.41 eV and 2.54 eV), the spectrum is dominated by three lines peaking at 0.9507, 0.9850, and 1.0053 eV and a double line with the maximum at 1.0307 eV. All these lines show replicas at a distance of 67 meV which equals the energy of the  $\text{A}_1(\text{TO})$  phonon in GaN [15]. They also exhibit similar temperature behavior. Therefore, we tentatively associate all of them with the same complex involving  $\text{Mn}^{4+}$  [5]. We also assume that these four resonances represent ZPL's because the distances between them do not match phonon energies of GaN, and local vibrational modes with center-specific energies should also produce higher order replicas. Hence, those lines represent the splitting of the ground state. At a magnitude of around 70 meV, such a splitting can only be explained by a reduction of the site symmetry within a complex consisting of the luminescence center and another defect (e.g., Mn-Mn pairs). A comparable splitting of the excited state would explain the absence of thermalization effects of these lines at temperatures up to 160 K (not shown).

At small excitation energies (e.g., 1.27 eV and 1.72 eV), three additional lines show up at 0.9975, 1.0113 and 1.0464 eV with replicas at 65.5, 65.2 and 69.6 meV, respectively. At higher temperatures the line at 1.0464 eV decreases in favor of a line at 1.0562 eV. On the basis of this thermalization we associate these two lines with one center and the other two at 0.9975 and 1.0113 eV with another in agreement with Ref. 5. While the distance of the latter two lines could be explained by a splitting caused by spin-orbit interaction, the absence of any thermalization at temperatures up to 160 K indicates either a strong splitting of the excited state caused by the formation of a complex or an unsplit excited state. We tentatively attribute the two lines at 1.0464 and 1.0562 eV to the  ${}^4\text{T}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F})$  transition of the isolated  $\text{Mn}^{4+}$  center. Arguments are the unsplit ground state and a splitting of the excited state that can be explained by spin-orbit coupling. As discussed above, the luminescence centers are excited selectively by below band gap excitation. At above band edge excitation, all of the previously discussed lines are present (compare Ref. 5). This observation suggests that the generation of free carriers represents an efficient excitation process for all of the observed centers.

The narrowest line at 1.0307 eV with a FWHM of 2.3 meV was studied by magneto PL spectroscopy. The magnetic field was varied between 0 and 5 T and the temperature between 2 and 40 K. However, as an effect of the magnetic field, we observed only a slight increase of the FWHM of around 20 %. Similar Zeeman shifts of ground and excited state in combination with



**Figure 2.** Excitation spectra of the two intense luminescence lines at 1.03 eV (Fig. 1) and the absorbance spectrum of  $\text{Mn}^{3+}$  in GaN on logarithmic scale.

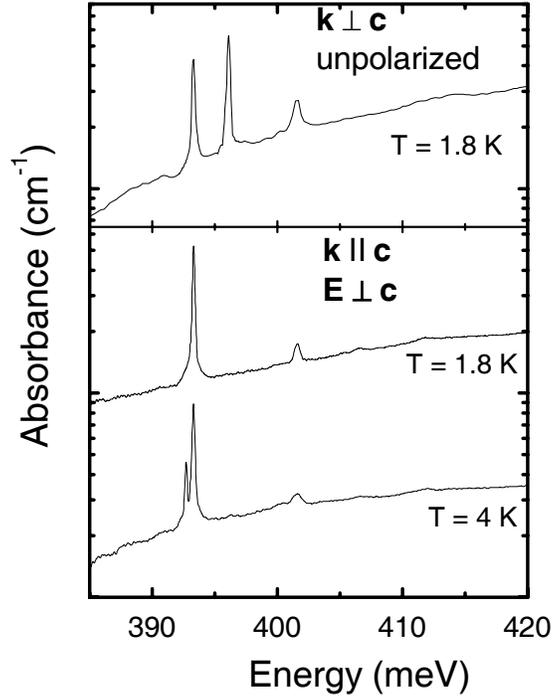
the relatively broad linewidth may be responsible for the absence of an observable Zeeman effect.

Figure 2 presents a comparison of two PLE spectra of the double line at 1.03 eV (dashed lines). One was recorded in our workgroup on the same sample as presented in Fig. 1. The other was published by Han et al. [7]. According to Ref. 7, the peaks at 1.8 and 2.3 eV represent internal  $\text{Mn}^{4+}$  transitions from the  ${}^4\text{T}_1(\text{F})$  ground state into the higher excited states  ${}^4\text{T}_1(\text{P})$  and  ${}^4\text{A}_2(\text{F})$ , respectively. These peaks are superimposed on a band representing the photoionization of a deep level which is approximated by the Lucovsky fit (dotted line) [7]. Han et al. interpret this photoionization as the charge transfer process  $\text{Mn}^{4+} \rightarrow \text{Mn}^{3+} + h_{\text{VB}}$ . They suggest that the subsequent recombination of  $\text{Mn}^{3+}$  with the hole results in the excited  $\text{Mn}^{4+}({}^4\text{T}_2(\text{F}))$  state [7]. This interpretation is questionable because it does not explain the absence of the alleged  $\text{Mn}^{4+}$  luminescence in undoped GaMnN samples. In such samples the stable charge state was shown to be  $\text{Mn}^{3+}$  [16] and holes generated by above band edge excitation should lead to the same recombination with  $\text{Mn}^{3+}$  as outlined in Ref. [7].

The major difference between the two PLE spectra is an additional excitation process that we observe at 1.5 eV. This additional peak may be caused by a different composition of our GaMnN:Mg sample. Alternatively, also light of a nearby peak may have been detected accidentally. Either way, we observe a strong resemblance to the internal  $\text{Mn}^{3+}({}^5\text{T}_2 \rightarrow {}^5\text{E})$  transition. The solid line in Fig. 2 is the absorbance spectrum of an undoped GaMnN sample grown under the same conditions. Two possible mechanisms may explain a potential involvement of the  $\text{Mn}^{3+}$  transition: (1) The energy resulting from the subsequent recombination

of  $\text{Mn}^{3+}$  is transferred to the nearby luminescent center (e.g., within a  $\text{Mn}^{3+}$ - $\text{Mn}^{4+}$  pair). (2) The recombination of excited  $\text{Mn}^{3+}$  with a free hole is more likely to result in the excited  $\text{Mn}^{4+}({}^4\text{T}_2(\text{F}))$  state.

Of course, we can not rule out that the resemblance with the  $\text{Mn}^{3+}$  absorption is mere coincidence. If this is the case, we would interpret the additional peak as the higher excited state  ${}^4\text{T}_1(\text{P})$  of  $\text{Mn}^{4+}$  involved in a different complex that was accidentally detected.



**Figure 3.** Polarized absorbance spectra of the internal  $\text{Fe}^{2+}$  transition ( ${}^5\text{E}$ — ${}^5\text{T}_2$ ) at 1.8 and 4 K.

The  $\text{Fe}^{2+}$  ion ( $3d^6$ ,  $L = 2$ ,  $S = 2$ ) has a  ${}^5\text{D}$  ground state. According to crystal field theory, the  ${}^5\text{D}$  is split by the impact of the tetrahedral crystal field into a  ${}^5\text{E}$  ground and  ${}^5\text{T}_2$  excited state separated by  $\Delta = 10|D_q| = 393$  meV in GaN [11]. Spin-orbit interaction causes the  ${}^5\text{E}$  state to split into five equidistant levels and the  ${}^5\text{T}_2$  state into six levels. A further splitting is caused by the slight deviation from tetrahedral symmetry in wurtzite GaN ( $C_{3v}$  symmetry) [17]. Moreover, a dynamical Jahn-Teller coupling to  $E$  phonon modes is likely to affect the fine structure [18, 19].

Figure 3 presents polarized absorbance spectra of the internal  $\text{Fe}^{2+}$  transition ( ${}^5\text{E}$ — ${}^5\text{T}_2$ ) at 1.8 and 4 K. The three observable lines at 1.8 K are found at the same positions as lines  $a$ ,  $b$  and  $q$  in Ref. 11 confirming that they represent transitions starting at the bottom level of the  ${}^5\text{E}$  state. Also the respective polarization of the lines is the same supporting the term scheme modeled on the basis of absorption spectra taken at 40 K [11]. Assuming that line ( $q$ ) at 401.6 meV represents the transition from the bottom ground state into the third allowed  ${}^5\text{T}_2$  state ( $\Gamma_3$ ) we can derive the energy separation between this state and the  $\Gamma_2$  state below to be 3.6 meV. At 4 K an additional line shows up 0.6 meV below the line at 393.3 meV. In accordance with the term scheme in Ref. 11, it represents the transition starting at the first excited  ${}^5\text{E}$  state  $\Gamma_2$  which becomes populated by thermal excitation.

In cubic crystals, a strong Jahn-Teller coupling was found to affect the  $\text{Fe}^{2+}({}^5\text{T}_2)$  state

resulting in numerous rather broad ZPL's that cannot be explained by crystal field theory alone [18]. In contrast, in Fig. 3, we observe only a few narrow lines that comply relatively well with crystal field theory. Hence, we conclude that unlike in cubic crystals, the  $\text{Fe}^{2+}({}^5\text{T}_2)$  center in the wurtzite GaN lattice is affected only weakly by a Jahn-Teller coupling. Here, the Jahn-Teller effect is probably quenched by the  $\text{C}_{3\text{V}}$  symmetry. This observation has been made before for the  $\text{Fe}^{3+}$  center in hexagonal GaN [9]. The impact of the Jahn-Teller effect on the  ${}^5\text{E}$  state is also weak which is in agreement with the situation in cubic crystals.

## CONCLUSIONS

The luminescence structure found in Mg co-doped GaMnN and associated with  $\text{Mn}^{4+}$  was analyzed by PL spectroscopy applying selective excitation. The presence of at least three different luminescence centers with different excitation behavior could be proven. The ZPL at 1.0464 eV is tentatively attributed to the  ${}^4\text{T}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F})$  transition of isolated  $\text{Mn}^{4+}$ . Vibrational replica were found at energies of  $\sim 67$  meV. PLE spectroscopy indicates that the internal  $d-d$  transition of  $\text{Mn}^{3+}$  may play an important role in the excitation process of the luminescence center. On the basis of magneto PL studies we assume equal  $g$  values for the ground and excited state. Despite the results presented here, we are not able to unambiguously confirm that the luminescence at 1 eV originates from  $\text{Mn}^{4+}$ .

Low temperature FTIR spectra of Fe doped GaN confirm the term scheme of the  $\text{Fe}^{2+}$  center in GaN as established in Ref. 11. Further insights into the fine structure of the  $\text{Fe}^{2+}({}^5\text{T}_2)$  were gained. Our results indicate that, in  $\text{C}_{3\text{V}}$  symmetry, the  $\text{Fe}^{2+}$  center is stabilized against Jahn-Teller coupling.

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