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Zeeman splittings of the $^5D_0$–$^7F_2$ transitions of Eu^{3+} ions implanted into GaN

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ABSTRACT

We report the magnetic field splittings of emission lines assigned to the $^5D_0$–$^7F_2$ transitions of Eu^{3+} centres in GaN. The application of a magnetic field in the *c*-axis direction (***B***||***c***) leads to a splitting of the major lines at 621 nm, 622 nm and 622.8 nm into two components. The Zeeman splitting is linear with magnetic field up to 5 Tesla for each line. In contrast, a magnetic field applied in the growth plane (***B***⊥***c***) does not influence the photoluminescence spectra. The estimated g-factors vary slightly from sample to sample with mean values of $g_{||}$ ~2.8, ~1.5 and ~2.0 for the emission lines at 621 nm, 622 nm and 622.8 nm respectively.

INTRODUCTION

When incorporated into crystalline hosts, trivalent rare earth (RE) ions exhibit narrow emission lines, ascribed to intra-*4f*-shell transitions, which are suitable for Zeeman studies at moderate magnetic fields [1]. Europium doping is particularly attractive for realisation of red light-emitting devices due to problems related to growth of InGaN with moderate InN fractions, also a potential source of red light. One advantage of using RE-doped material in light-emitting devices is the temperature independence of the spectral position of the emission lines due to the shielding of *4f* electrons by outer $5s^2$ and $5p^6$ electrons [2]. In widegap semiconductors, RE emission intensity is also expected to show improved temperature stability [3].

Eu^{3+} ions in GaN produce red emission, around 621 nm, assigned to the $^5D_0$–$^7F_2$ intra *4f*-shell transition [4]. A GaN:Eu red LED was recently reported and analysed[5].

EXPERIMENT

GaN templates were grown on (0001) sapphire substrates by Metal Organic Chemical Vapour Deposition (MOCVD). Eu^{3+} implantation at 300 keV was performed in random orientation to fluences of 10^{13} and 10^{15} cm^{-2}. After implantation samples were annealed for 30 minutes at temperatures ranging from 1000 to 1450 °C in a nitrogen atmosphere at a pressure of 10^4 bar. The samples were subsequently mounted in a continuous flow helium cryostat. Low temperature photoluminescence (PL) spectra were excited at 325 nm by a He-Cd laser. A magnetic field of up to 5 Tesla was applied using a superconducting split-coil magnet. A Jobin-Yvon 3000 triple grating spectrometer dispersed the emitted light and a CCD camera detected the PL signal.

Figure 1 shows Zeeman splittings of the $^5D_0$-$^7F_2$ transitions of Eu^{3+} ions in GaN. The maximum splitting occurs with the magnetic field applied along the *c*-axis of the crystal. No Zeeman splitting was observed when the magnetic field was applied perpendicular to the *c*-axis.

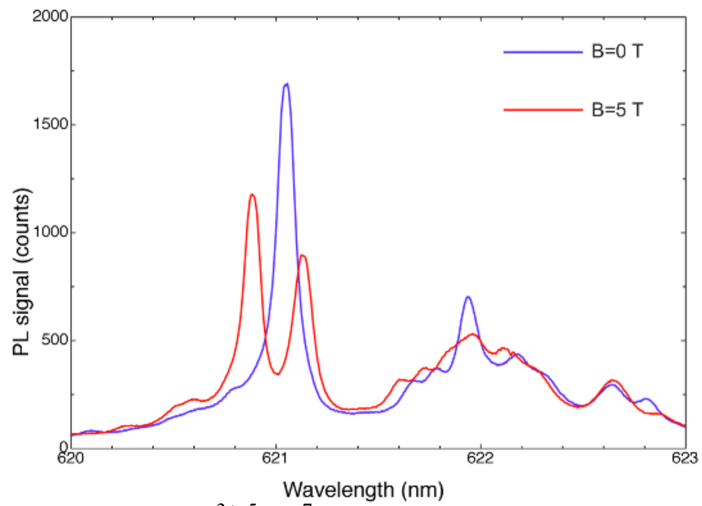

Figure 1. Zeeman splittings of the Eu^{3+} $^5D_0$-$^7F_2$ lines in a magnetic field applied with ***B*||*c***.

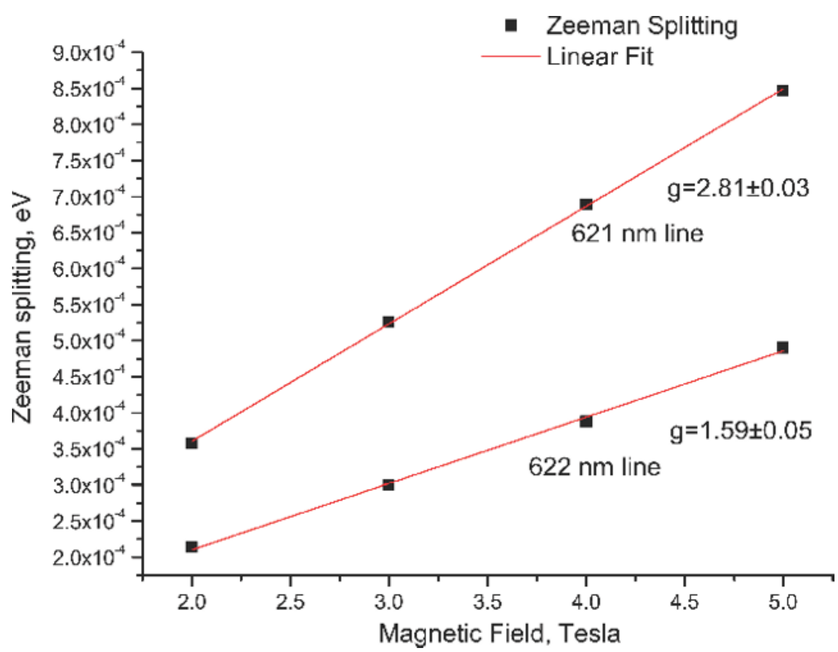

Figure 2. Dependence of Zeeman splitting energy on magnetic field for 621 nm and 622 nm lines.

Figure 2 shows the dependence of the Zeeman splitting on magnetic field for lines at 621 nm and 622 nm. The dependence on field is linear and corresponding g-factors are estimated to be $g_{||}$=2.81±0.03 and $g_{||}$=1.59±0.05 for emission lines at 621 nm and 622 nm respectively for this sample. Interestingly, the g-factors were found to vary a little from sample to sample. A sample from the same set, but implanted to a lower fluence, exhibited $g_{||}$-factors of 2.63±0.02 and 1.62±0.36 for emission lines at 621 nm and 622 nm respectively. The weaker emission line at 622.8 nm also splits, with a g-factor of ~2.0.

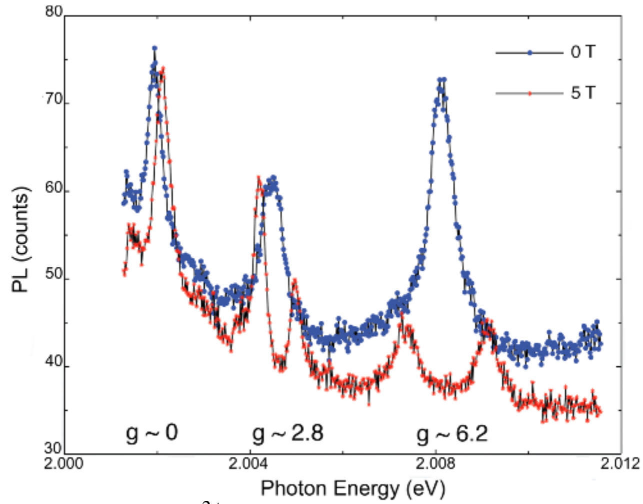

Figure 3. The splitting of the minor Eu^{3+} emission lines at 617.5 nm (~2.009 eV) and 618.4 nm (~2.005 eV). The line near 619 nm (2.002 eV) shifts to higher energy but does not split.

Figure 3 shows that the minor lines at 617.5 nm and 618.4 nm also split in a magnetic field with g-factors of ~6.2 and ~ 2.8 respectively. Note that the g-factor for the final $^7F_2$ state of a $^5D_0$-$^7F_2$ transition is exactly 1.5 according to the well-known Landé formula [1]. The angular dependences of the Zeeman splittings for two samples are combined in Figure 4 using two measurements starting from $\boldsymbol{B}\|\boldsymbol{c}$ and $\boldsymbol{B}\perp\boldsymbol{c}$ orientations. The data follow the $g = g_{\|}\cos\theta$ dependence corresponding to the assumption $g_{\perp}=0$.

Figure 5 shows that all Eu^{3+} Zeeman components emission lines are partially polarized. The g-factors were found to be negative on the basis of the spectral positions of σ+ and σ- components. Attempts to measure optically detected magnetic resonance (ODMR) originating from a proposed excitation transfer mechanism involving Eu^{2+} intermediate state [6] or an intrinsic defect [7] were unsuccessful. However, conventional ODMR would not be sensitive to fast energy transfer processes ($\tau \leq 1$ μs) involving free or bound excitons.

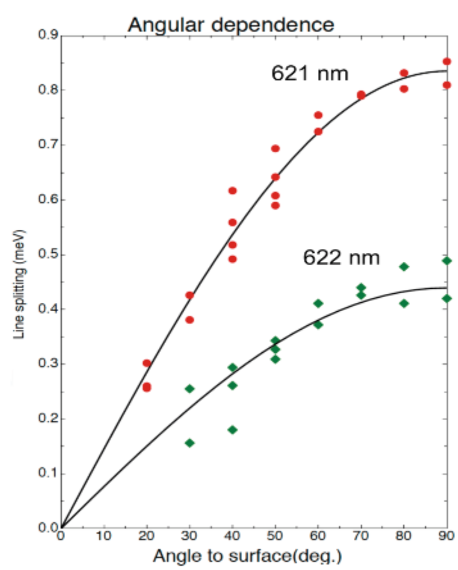

Figure 4. Angular dependence of Zeeman energy splittings for 621 and 622 nm lines (data for two samples combined). The lines are fits to $g = g_{\|}\cos\theta$. See text.

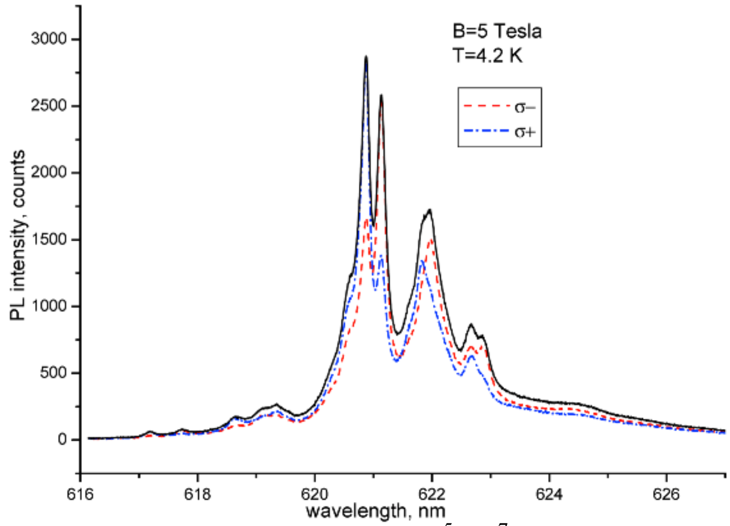

Figure 5. Polarization of Zeeman split components of $^5D_0$-$^7F_2$ emission lines.

DISCUSSION

Recent optical studies of GaN epilayers implanted with Eu^{3+} ions suggest that two main optically active Eu^{3+} centres, labelled Eu1 and Eu2, can be excited via the host [6, 8]. Eu2, with its principal line at 621 nm, can be excited predominantly with light having energy above the bandgap, whereas Eu1 (principal line at 622 nm) can be excited with both below- and above-bandgap light. The Eu2 centre is identified with Eu^{3+} ions occupying Ga sites in GaN whereas Eu1 is ascribed to Eu^{3+} ions on a Ga site with an adjacent lattice defect [7]. Eu1 and Eu2 spectral features are identified in Figure 6.

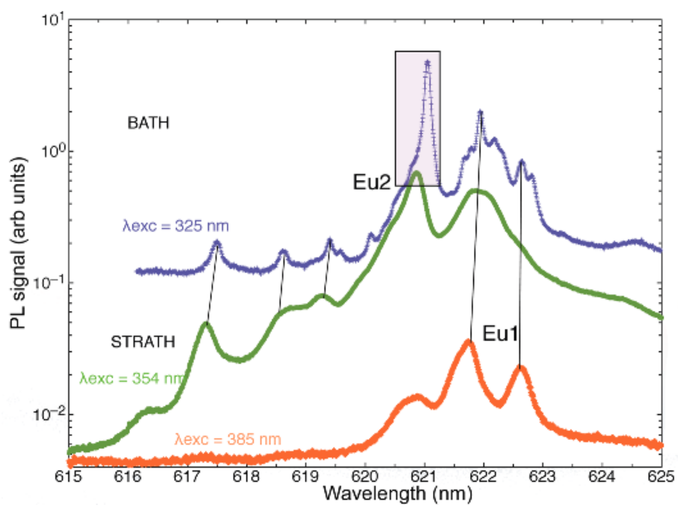

Figure 6. Comparison of PL spectra for the same sample measured at the University of Bath and the University of Strathclyde. Eu1 and Eu2 features can be distinguished using above-and below-gap excitation as indicated. The Bath spectra show a superposition of both sets of lines.

The PL studies in magnetic field reported in this paper produce more questions than answers about the nature of the optically active Eu^{3+} centres in GaN. Apart from different g-factors for Eu1 and Eu2 centres, we find that different lines originating on the same centre (i.e. those at 622 nm and 622.8 nm) split differently in a magnetic field. The Zeeman splittings observed in the dominant PL spectra of GaN:Eu must originate in the final state of the transition i.e. the $^7F_2$ state, since the excited $^5D_0$ state does not have an associated magnetic moment and the ODMR experiments failed to detect any spin-dependent response.

It is interesting to note that recent theoretical calculations predict substitutional Eu on Ga to produce a deep acceptor state [8]. The highly anisotropic g-factors of Mg-related acceptor states in GaN were explained by diminished influence of the crystal field in the basal plane when the acceptor becomes shallower and holes become less localized [9].

Finally, the experimental results open up the possibility of selective optical excitation and manipulation of the magnetic moments in the $^7F_2$ state of Eu1 and Eu2 centres in GaN.

CONCLUSIONS

Magneto-PL studies highlight, once again, the complex nature of Eu^{3+} optically active centers in GaN. Not only do emission lines for Eu1 and Eu2 centres split differently in a magnetic field parallel to the c-axis but emission lines belonging to the same center also split differently. The observed Zeeman splittings are associated with magnetic moments of the final $^7F_2$ state of the $^5D_0$-$^7F_2$ transition.

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