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# Eu–Mg defects and donor–acceptor pairs in GaN: photodissociation and the excitation transfer problem

A K Singh<sup>1</sup>, K P O'Donnell<sup>1</sup>, P R Edwards<sup>1</sup>, K Lorenz<sup>2</sup>, J H Leach<sup>3</sup> and M Boćkowski<sup>4</sup>

<sup>1</sup> SUPA Department of Physics, University of Strathclyde, 107 Rottenrow, Glasgow G4 0NG, Scotland, United Kingdom

<sup>2</sup> IPFN, Instituto Superior Técnico, Universidade de Lisboa, Campus Tecnológico e Nuclear, Estrada Nacional 10, 2695-066 Bobadela LRS, Portugal

<sup>3</sup> KYMA Technologies, 8829 Midway West Rd, Raleigh, NC 27612, United States of America

<sup>4</sup> Institute of High Pressure Physics PAS, Sokolowska 29/37, 01-142 Warsaw, Poland

E-mail: [k.p.odonnell@strath.ac.uk](mailto:k.p.odonnell@strath.ac.uk)

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## Abstract

We have investigated the temperature-dependent photoluminescence (TDPL) profiles of  $\text{Eu}^{3+}$  ions implanted in an HVPE-grown bulk GaN sample doped with Mg and of donor–acceptor pairs (DAP) involving the shallow Mg acceptor in GaN(Mg) (unimplanted) and GaN(Mg):Eu samples. Below 125 K, the TDPL of  $\text{Eu}^{3+}$  in GaN(Mg):Eu correlates with that of the DAP. Below 75 K, the intensity of  $\text{Eu}^{3+}$  emission saturates, indicating a limitation to the numbers of Eu–Mg defects available to receive excitation transferred from the host, while the DAP continues to increase, albeit more slowly in the implanted than the unimplanted sample. Prolonged exposure to UV light at low temperature results in the photodissociation of Eu–Mg defects in their  $\text{Eu1(Mg)}$  configuration, with a corresponding increase in shallow DAP emission and the emergence of emission from unassociated  $\text{Eu}_{\text{Ga}}$  (Eu2) defects.

Keywords: photoluminescence, energy transfer, gallium nitride, rare earth


 Supplementary material for this article is available [online](#)

(Some figures may appear in colour only in the online journal)

## 1. Introduction

Rare-earth (RE)-doped wide bandgap semiconductors have potential applications in light emitting diodes and display devices [1–4]. When incorporated in III-nitride semiconductors,  $\text{RE}^{3+}$  ions exhibit characteristic sets of sharp *intra-4f shell* emission lines; Eu-doped GaN attracts special attention for intense red emission near 621 nm, due to  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  multiplet transitions [5–10]. In recent years, a number of studies have shown that Mg co-doping of GaN:Eu significantly

increases the luminescence intensity of samples measured at room temperature [11, 12]. For example, Sekiguchi *et al* have compared the quantum efficiencies of GaN:Eu and GaN(Mg):Eu samples which were found to be 6.8% and 77%, respectively [13]. In the absence of Mg, Eu-implanted GaN features two main luminescence centres, which we call Eu2 ( $\text{Eu}_{\text{Ga}}$ , the unassociated ‘prime’ defect [14]) and Eu1 ( $\text{Eu}_{\text{Ga-X}}$ , where X is a lattice defect, possibly a nitrogen vacancy [8]). In contrast to GaN:Eu, which shows  $\text{Eu}^{3+}$  emission from many different ‘RE sites’ [15], the photoluminescence (PL) spectrum of *ion-implanted* GaN(Mg):Eu is apparently dominated by emission from a single, albeit photochromic centre with a unique set of emission lines at room temperature, labelled Eu0 [9]; a variety of experimental results indicates that the Eu0

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defect comprises a single Mg atom in close association with an Eu2 defect [9, 16].

The luminescence of  $\text{Eu}^{3+}$  is often excited *indirectly* through energy transfer (ET) from the GaN host, necessarily so in electroluminescence (EL) applications, but also by photoexcitation with above-bandgap or near-bandgap light [6]; several mechanisms for ET have been proposed: ‘RE-defect’-related Auger excitation [17, 18]; excitation through charge transfer states of  $\text{Eu}^{3+}/\text{Eu}^{2+}$  ions [19–21]; excitation via bound excitons [22]. Mishra *et al* [23] proposed ET from donor–acceptor pairs (DAP) to  $\text{Eu}^{3+}$ ; Mitchell *et al* [8] further speculated that ET from DAP, formed either by unintentionally doped oxygen  $\text{O}_\text{N}$  and  $\text{V}_\text{Ga}$ , or by  $\text{V}_\text{N}$  and  $\text{V}_\text{Ga}$ , might be responsible for emission from Eu2 and Eu1 defects, respectively. However, to the best of our knowledge, there is only a single report [24] that provides *spectroscopic* evidence of deep-level interaction with  $\text{Eu}^{3+}$  by demonstrating the below-gap photoluminescence excitation (PL/E) of a single sample.

In this paper, we have investigated and compared TDPL of  $\text{Eu}^{3+}$  ions in GaN(Mg):Eu and of DAP in GaN(Mg) and GaN(Mg):Eu. Our investigation shows that below 125 K, TDPL of  $\text{Eu}^{3+}$  in GaN(Mg):Eu correlates with that of the DAP, suggesting a competition between DAP emission and excitation transfer to  $\text{Eu}^{3+}$  ions. Prolonged UV light exposure at low temperature partially converts Eu–Mg centres to Eu2 through light-induced Mg migration. The Eu–Mg centres recover to a great extent after sample reannealing.

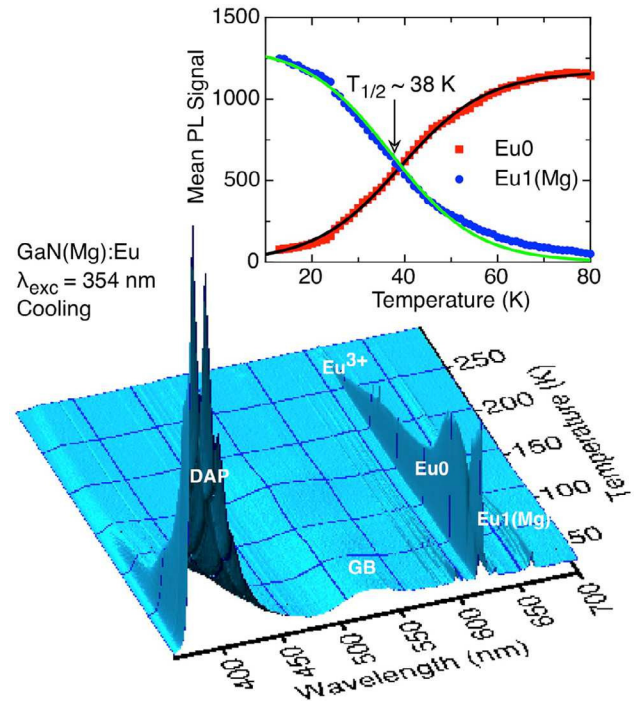
## 2. Methods

### 2.1. Sample preparation

A freestanding Mg-doped GaN sample, measuring  $1\text{ cm} \times 0.4\text{ cm} \times 0.5\text{ mm}$ , was grown by hydride vapour phase epitaxy (HVPE) at Kyma Technologies, USA. The Mg doping level, measured by secondary ion mass spectrometry, averages  $3 \times 10^{18}\text{ Mg cm}^{-3}$ . In addition to Mg, the sample is also unintentionally doped with Si to a concentration of  $\sim 1 \times 10^{15}\text{ atoms cm}^{-3}$ . The concentrations of other unintentional dopants, for example, O, H and Fe, were below the detection limits of SIMS. The sample was implanted with Eu ions along the surface normal to a fluence of  $2 \times 10^{13}\text{ cm}^{-2}$  @ 300 keV, resulting in a maximum Eu concentration,  $\sim 50\text{ nm}$  below the surface, of  $\sim 3 \times 10^{18}\text{ cm}^{-3}$ , closely matching the mean Mg level. To repair implantation damage, the sample was annealed at high temperature and pressure (HTHP): 1673 K, 10 GPa of  $\text{N}_2$ ; during annealing, the sample surfaces were covered with bulk GaN powder to prevent the out-diffusion of nitrogen.

### 2.2. Optical measurements

Samples were mounted in a closed-cycle helium cryorefrigerator with base temperature of 12.5 K. TDPL spectra of GaN(Mg) and GaN(Mg):Eu were recorded during the cooling cycle at a 1 K temperature interval with a cooling rate of  $\sim 6\text{ K min}^{-1}$ . PL excitation used either a 355 nm CW laser (with maximum power of 20 mW in a 1.5 mm spot) or a 1 kW Xe



**Figure 1.** Temperature-dependent PL spectra of GaN(Mg):Eu during a cooling run. The inset figure shows the mean PL signal intensities of  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transitions of  $\text{Eu}^{3+}$  for Eu0 and Eu1(Mg) configurations of the Eu–Mg defect as a function of temperature.

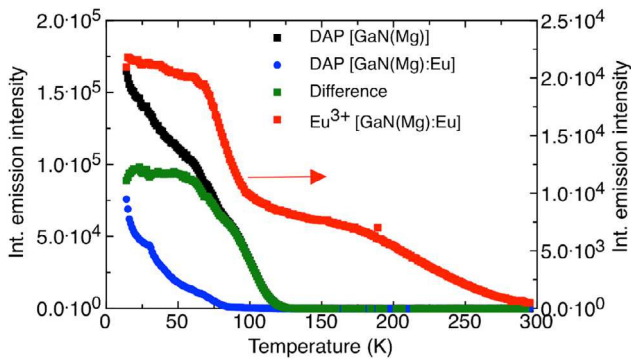
lamp filtered through a  $\frac{1}{4}$ -m monochromator with  $\lambda_{\text{exc}} = 350, 354$  and  $362\text{ nm}$ . Luminescence was dispersed using two monochromators (Andor Shamrock (model No.: SR-163) and McPherson (207)) in order to capture emission over the full visible range (350–750 nm) and in a 15 nm window around 622 nm, resolving the closely spaced  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  emission lines from  $\text{Eu}^{3+}$  ions in different defects/defect configurations. Spectra were recorded using cooled  $1024 \times 127$  pixel CCD cameras with effective spectral resolutions of about 1 nm and 0.04 nm, respectively and digital (pixel) resolutions of 0.4 nm and 0.015 nm, respectively.

## 3. Results

### 3.1. TDPL of Eu–Mg defects in GaN(Mg):Eu

Figure 1 shows the TDPL spectra of the GaN(Mg):Eu sample recorded during a cooling run from 295 to 14 K under 354 nm,  $8\text{ mW cm}^{-2}$  excitation, corresponding to a photon flux of  $2 \times 10^{16}\text{ cm}^{-2}\text{ s}^{-1}$ . The RT PL spectrum comprises a weak near-band-edge emission, with a wavelength peak of  $\sim 383\text{ nm}$  (3.24 eV), a green emission band, peaking at  $\sim 530\text{ nm}$  (2.34 eV), corresponding to native GaN lattice defects, and strong  $\text{Eu}^{3+}$  emission from the Eu0 defect, with its main peak at 618.9 nm (2.004 eV).

In the temperature range from 295 K to base temperature, the intensity of all bands and lines increases because of decreased non-radiative competition for the available excitation. Below 125 K, DAP luminescence corresponding to shallow donors and acceptors appears with a zero-phonon line at 379.3 nm (3.27 eV) and prominent LO-phonon replicas

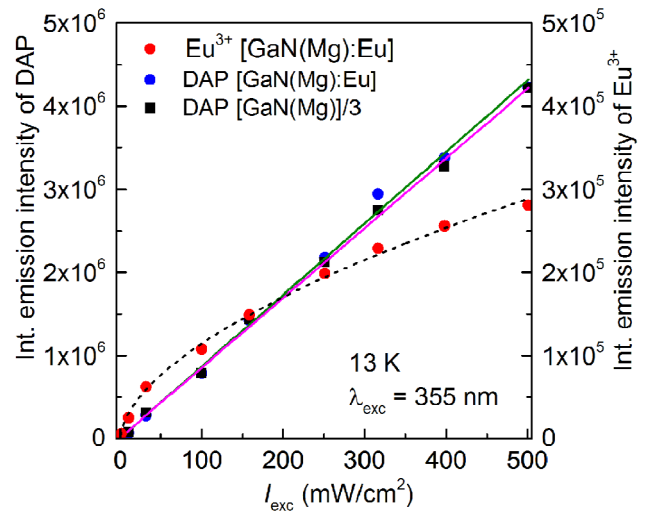


**Figure 2.** TDPL profiles of DAP in GaN(Mg) and GaN(Mg):Eu as a function of temperature, recorded using 354 nm excitation during a cooling run. The difference between these temperature profiles correlates with that of the  $\text{Eu}^{3+}$  in GaN(Mg):Eu below 100 K (see text).

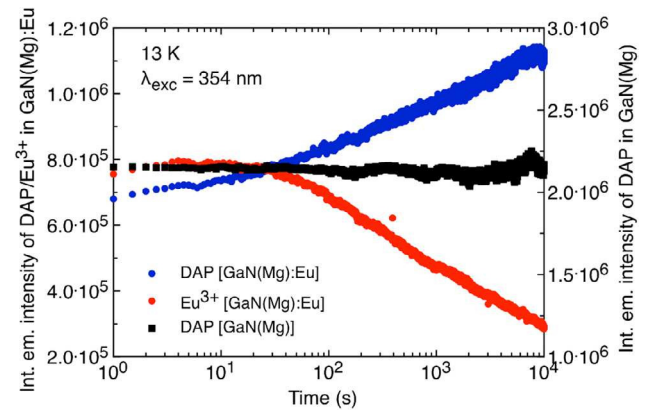
at 390 and 402 nm (3.18 and 3.09 eV). Upon further cooling, below  $\sim 50$  K,  $\text{Eu}0$  switches to  $\text{Eu}1(\text{Mg})$  with a main peak at 621.8 nm (1.997 eV) [9, 25]. ( $\text{Eu}1(\text{Mg})$  is different from the common  $\text{Eu}1$  defect; it comprises a Mg atom in close association with Eu and, unlike  $\text{Eu}1$ , it does not show a sub-gap excitation band [20].) To illustrate this *photochromic* switching, the inset to figure 1 plots the mean spectral intensities of  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  emission lines of the  $\text{Eu}0$  and  $\text{Eu}1(\text{Mg})$  for the GaN(Mg):Eu sample (recorded at higher resolution than figure 1) as a function of temperature. Cooling the sample below 75 K results in a rapid decrease in  $\text{Eu}0$  while the  $\text{Eu}1(\text{Mg})$  signal rises to replace it.  $T_{1/2} \sim 38$  K marks the temperature at which the defects are ‘half-switched’. In previous publications [9, 16, 25], we have reported that switching between  $\text{Eu}0$  and  $\text{Eu}1(\text{Mg})$  demonstrates the structural instability of GaN(Mg) at low temperature, with Eu ions acting as sensitive nanoprobe of the local environment. In a previous publication, ([25] and references therein) we also considered two other models advanced in the literature to explain temperature dependent PL of  $\text{Eu}^{3+}$  in GaN(Mg). We ruled them out, mainly because of their inadequacy in explaining the emission behaviour during both the cooling and warming runs; details can be found in [25].

### 3.2. Comparing TDPL profiles of DAP and total $\text{Eu}^{3+}$

Figure 2 compares the TDPL profiles of several emission signals recorded during cooling: (1) the wavelength-integrated emission intensities of DAP from GaN(Mg); (2) the integrated emission intensities of DAP from GaN(Mg):Eu; (3) the difference of integrated emission intensities of DAP from GaN(Mg) and GaN(Mg):Eu (i.e. (3) = (1)–(2)); and (4) the integrated intensities of  $\text{Eu}^{3+}$  emissions from GaN(Mg):Eu (=  $\text{Eu}0 + \text{Eu}1(\text{Mg}) + \text{Eu}2$  (see later)). (Above 50 K, samples also show weak emission corresponding to  $e\text{-A}^\circ$  recombination (see figure S1 in the supporting information ([stacks.iop.org/JPhysD/51/065106/mmedia](http://stacks.iop.org/JPhysD/51/065106/mmedia))) which overlaps the DAP zero-phonon line; hence the wavelength-integrated emission intensities of DAP include emission corresponding to  $e\text{A}^\circ$ ). For unimplanted GaN(Mg), the DAP emission increases rapidly below 125 K; for GaN(Mg):Eu the rate



**Figure 3.** Excitation power dependences of DAP and  $\text{Eu}^{3+}$  emissions under 355 nm excitation at 13 K. Solid lines show linear fits to DAP emission in GaN(Mg):Eu and GaN(Mg) samples, whereas the dotted line shows a square-root fit to  $\text{Eu}^{3+}$  emission in GaN(Mg):Eu.



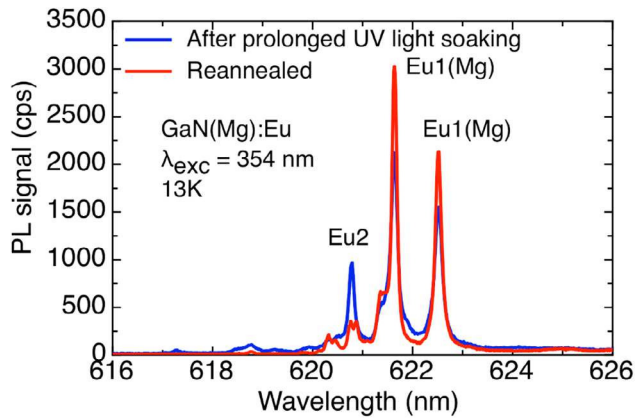
**Figure 4.** Integrated intensities of DAP and  $\text{Eu}^{3+}$  emission as a function of time, recorded at 13 K using 354 nm excitation ( $I_{\text{exc}} = 8 \text{ mW cm}^{-2}$ ) on GaN(Mg):Eu and GaN(Mg) samples.

of increase is somewhat moderated. While the  $\text{Eu}^{3+}$  TDPL saturates below  $\sim 75$  K, that of the DAP continues to increase. The *difference* between the two DAP profiles is similar to the temperature profile of  $\text{Eu}^{3+}$  emission, suggesting that the DAP excitation ‘missing’ in GaN(Mg):Eu transfers in some way to  $\text{Eu}^{3+}$ .

Figure 3 shows the wavelength-integrated intensities of DAP and  $\text{Eu}^{3+}$  emissions as functions of excitation density at 13 K. Both dependences seem anomalous: the DAP emission increases *linearly* in both the implanted and unimplanted samples while total  $\text{Eu}^{3+}$  emission shows an approximate square-root dependence on excitation power.

### 3.3. UV light-induced photo-dissociation of Eu–Mg defects

To study any light-induced alteration in emission spectra, as expected from previous studies [26], we stabilised the sample in the dark at the base temperature of the cryostat for 30 min, and recorded a kinetic series of PL spectra at intervals of 0.5 s



**Figure 5.** Comparison of the PL spectra corresponding to  ${}^3D_0 \rightarrow {}^7F_2$  transitions of  $\text{Eu}^{3+}$  ions from prolonged UV-soaked, and reannealed GaN(Mg):Eu samples at 13 K, showing recovery of the Eu–Mg defect after reannealing.

during continuous illumination from time zero. Figure 4 shows that the wavelength-integrated intensity of the DAP emission in *unimplanted* GaN(Mg) remains constant, ignoring small lamp fluctuations over the long experimental duration. On the other hand, for the Eu-implanted sample, the integrated emission intensity of the DAP *increases* as that of  $\text{Eu}^{3+}$ , mainly due to the fact that Eu1(Mg) near base temperature *decreases*. Light soaking also produces fundamental changes in the spectrum (figure 5). After repeated and prolonged UV light soaking at low temperature, the intensity of the line corresponding to Eu2 defects at 620.8 nm grows from near-zero to a substantial fraction of that of the Eu1(Mg) defect at 621.7 nm.

#### 4. Discussion

With the abrupt rise of intensity in the temperature range 150–100 K, figure 1 shows an experimental correlation, at least, between DAP and  $\text{Eu}^{3+}$  emission in GaN(Mg):Eu. At higher temperatures, where DAP emission is absent, we must look for another process to increase the  $\text{Eu}^{3+}$  signal; this may be due to reduced competition from non-radiative processes [27, 28]. The inset to figure 1 shows Eu0 *switching* to Eu1(Mg) below  $\sim 75$  K. In previous publications, we have described this one-to-one transformation as a nanoscale phase instability [9, 16, 25]. We proposed that at low temperatures, localisation of holes on the axial N neighbours of Mg atoms drives a lattice distortion that increases Eu–Mg separation [25]. Sample warming above 150 K, not shown here, triggers the release of holes by Mg acceptors. Eu0 reappears as the lattice relaxes locally to its starting configuration [16, 25].

The difference in DAP TDPL profiles of GaN(Mg) and GaN(Mg):Eu samples shown in figure 2 suggests that the addition of  $\text{Eu}^{3+}$  ions introduces a new physical process that impacts upon the emission intensity. In particular, the difference profile, obtained by subtracting that of GaN(Mg):Eu DAP from that of GaN(Mg), closely resembles that of the  $\text{Eu}^{3+}$  emission below 125 K, implying that the additional physical process could be an ET from DAP to  $\text{Eu}^{3+}$  ions. On

the other hand, simple competition between independent excitation paths would lead to the same result. Above 125 K, since there is no DAP emission, the excitation transfer might occur via the several different processes suggested in the introduction. Our group previously suggested a possible excitation route through the charge transfer states of Eu ions [20].

A striking feature of figure 2 is the saturation of difference profile and the  $\text{Eu}^{3+}$  temperature profile below  $\sim 75$  K. This limiting behaviour is further observed in the integrated emission intensity versus impinging light intensity plots shown in figure 3, which depicts a square-root and linear dependence for  $\text{Eu}^{3+}$  ions and DAP emission intensities, respectively. Since the thickness of the GaN(Mg) sample is  $\sim 0.5$  mm and  $\text{Eu}^{3+}$  ions are implanted only within 100 nm of the surface, saturation of  $\text{Eu}^{3+}$  emission indicates the presence of a limited number of Eu–Mg pairs to receive excitation from any active channel. It is important to recall that Eu implantation results in a non-uniform concentration profile with a peak concentration of  $\sim 3 \times 10^{18} \text{ cm}^{-3}$  (closely matching the mean Mg level)  $\sim 50$  nm below the surface. A simple analysis suggests that  $\sim 50\%$  of the Mg atoms in the implanted region are not associated with Eu atoms. Furthermore, at 355 nm excitation,  $\sim 37\%$  of incident photons penetrate to depths (beyond 100 nm) where Eu is hardly present. As the penetration depth is not a steep function of photon energy above the band gap, the use of available shorter wavelengths might not create a significant difference in Eu and DAP emission versus excitation intensity plots. In order to study the effect of excitation penetration depth on Eu and DAP emission, we recorded PL using 362 and 350 nm excitation (respectively slightly below and slightly above the band gap) at 13 K. Figure S2 of the supporting information reveals that the PL intensity versus the excitation intensity plot show the same square-root and linear dependence for  $\text{Eu}^{3+}$  ions and DAP emission intensities, respectively. Noticeably, as 362 nm photons penetrate deeper in the sample, the integrated emission intensity of DAP is higher than observed for 350 nm excitation, whereas the reverse is true for Eu emission.

Figure 4 reveals that prolonged UV light soaking at 13 K causes a decrease in emission intensity of  $\text{Eu}^{3+}$  (mainly of Eu1(Mg) at this low temperature) and a simultaneous increase in DAP emission intensity, once more suggesting a competition between DAP and  $\text{Eu}^{3+}$  excitation. The accompanying spectral changes, with the emergence of the characteristic Eu2 line, suggests strongly that prolonged exposure to UV light causes photo-dissociation of Eu–Mg pairs with the direct consequence, at least in part, of producing Eu2 defects. This conjecture finds support in a further experimental result shown in figure 5. After reannealing the sample at high temperature and high pressure, the PL of Eu2 defects decreases while that of Eu1(Mg) is partially restored, clearly indicating the recovery of Eu–Mg defects, through the *re-association* of Eu and Mg ions, upon HTHP reannealing. These findings are entirely consistent with the model that Eu0 and Eu1(Mg) configurations comprise a Eu atom in close association with a Mg acceptor [9, 16, 25].

## 5. Summary and conclusions

The RT PL spectrum of ion-implanted HVPE Kyma GaN(Mg):Eu shows band-edge emission, a green emission band corresponding to native GaN lattice defects and  $\text{Eu}^{3+}$  emission from Eu0 defects, all of which increase in intensity on sample cooling. Cooling below 125 K elicits DAP emission with LO-phonon replicas. Upon further cooling below 75 K, Eu–Mg defects *switch configuration* from Eu0 to Eu1(Mg) and the total  $\text{Eu}^{3+}$  emission saturates. The difference in the TDPL of DAP in GaN(Mg) and GaN(Mg):Eu, which matches the profile of  $\text{Eu}^{3+}$  emission, may suggest excitation transfer from DAP to  $\text{Eu}^{3+}$  ions or simple competition between the two processes. Continuous UV light soaking at 13 K leads to photo-dissociation of Eu–Mg pairs, resulting in the appearance of Eu2 and a simultaneous increase in DAP emission. After prolonged UV soaking, a sample can be partially restored by re-annealing at HTHP: in line with the results of recent structural studies [29], Mg appears to be a *labile* defect in GaN.

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## ORCID iDs

A K Singh  <https://orcid.org/0000-0001-7924-8700>  
 K P O'Donnell  <https://orcid.org/0000-0003-3072-3675>  
 P R Edwards  <https://orcid.org/0000-0001-7671-7698>

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