Optically detected magnetic resonance of paired defects in as-grown magnesium-doped GaN

J. John Davies, G. N. Aliev, S. J. Bingham, D. Wolverson,* S. Stepanov, B. Yavich, and W. N. Wang
Department of Physics, University of Bath, Bath BA2 7AY, United Kingdom
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Optically detected magnetic-resonance experiments on as-grown magnesium-doped GaN produced by metal-organic vapor phase epitaxy reveal the presence of a triplet state spectrum with a zero-field splitting that corresponds to a pair of centers, each with a spin of 1/2, strongly coupled by an exchange interaction and separated in the direction of the *c* axis by 0.26 nm. The spectra show no resolved hyperfine structure, suggesting that the centers involve elements with zero nuclear spin. The separation of 0.26 nm corresponds to the distance between two octahedral interstitial sites, suggesting that the spectrum is due to an interstitial-interstitial pair, possibly involving magnesium and oxygen.

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I. INTRODUCTION

Despite the success of GaN and its alloys as constituents of blue-emitting laser devices there is still considerable uncertainty about the role of defects in controlling the optoelectronic behavior. Of particular interest is the behavior at the atomic level during the procedures used to grow *p*-type material of low resistivity. The most successful *p*-type dopant is magnesium, with hole concentrations approaching 10^{18} cm^{-3} being attained in layers grown by metallo-organic vapor phase epitaxy (MOVPE) and subsequently annealed in nitrogen atmospheres;[1,2] hole concentrations in excess of 10^{18} cm^{-3} may be achievable using special techniques such as superlattice doping[3] or co-doping.[4] The annealing process itself is not understood but is often presumed to involve relocation of the hydrogen atoms which are inevitably present in as-grown MOVPE layers and which are believed to passivate the magnesium acceptors.[5] It has also been suggested that the mechanisms by which the acceptors are activated during annealing involve oxygen, which is often present at high levels in MOVPE material[6] and which may therefore lead to compensation of acceptor dopants. To study this complicated problem, several approaches have been used, including photoluminescence, electrical and thermal measurements, augmented by a series of theoretical investigations of the formation energies, stabilities, and electrical properties of a range of potential defect structures. A particular technique that links experimental data concerning the symmetries and possible structures of defect centers to the possible models predicted theoretically is electron spin resonance (ESR), which, for epitaxial layers, is usually carried out using optical detection (for a review see, e.g., Ref. 7; for work on GaN:Mg, see, e.g., Ref. 8). In the present paper we describe the results of such experiments on magnesium-doped GaN layers produced by MOVPE. We observe spectra that appear not previously to have been reported and which provide direct evidence for the pairing of defects in as-grown material.

II. EXPERIMENTAL DETAILS

A. Details of the specimens

The GaN layers were grown on *c*-plane sapphire substrates by MOVPE in an Aixtron HT200 reactor using trimethylgallium (TMGa) or triethylgallium (TEGa), bis cyclopentadienyl magnesium (Cp_2Mg), diethylzinc (DEZn), and ammonia (NH_3) precursors. Further details of the growth conditions are given in Table I. In all cases, the metallo-organic to hydride ratio was 0.2, the V/III ratio was 1705, and the growth temperature was 1070 K. Also in all cases, a buffer layer of nominally undoped GaN was first deposited, followed by a compensated layer of zinc-doped material and then the magnesium-doped material. In a given specimen, these layers were typically of respective thicknesses 0.8, 0.8, and 0.5 μm. From secondary-ion mass spectrometry measurements, the magnesium concentrations were determined to be in the range 10^{19}–10^{20} cm^{-3}. The present investigation was concerned primarily with as-grown specimens. However, following annealing in nitrogen at atmospheric pressure at 800 °C for periods of 10–30 min, room-temperature hole densities p in the region of 10^{17}–10^{18} cm^{-3} were obtained (as measured by Hall experiments).

B. ODMR technique

Optically detected magnetic resonance (ODMR) has been used for many years to investigate recombination processes in semiconductors. The key feature is that the recombination often involves spin selection rules, so that the characteristics of the accompanying photoluminescence (intensity, polarization) are in some way dependent on the spin distribution within the states that participate directly in (or in some other way affect) the recombination processes. In the simplest case, increases in the intensity of the photoluminescence (PL) are observed when magnetic resonance occurs in the excited state, but in GaN the behavior is often observed to be more complicated, with magnetic-resonance signals being observed from levels that are involved in recombination processes that are in competition with the PL that is being monitored and therefore appearing as decreases in the emitted intensity. In magnesium-doped GaN, both positive (PL enhancing) and negative (PL quenching) ODMR signals have been reported and a recent account has been given in Ref. 8, which contains references to earlier work.

The present investigation was carried out with microwaves at a frequency of 13.7 GHz and power ~50 mW with the specimen in direct contact with superfluid helium in a

TABLE I. Characterization data of the four samples investigated; the Cp_2Mg flow rate, resistivity, Hall mobility, carrier concentration after annealing, and standard growth conditions are specified. Note that the fourth sample contained the lowest amount of Mg and remained *n* type after annealing.

Growth run	Mg flow, nmol/min	ρ, Ω cm	μ, $cm^2/V\,s$	*n* or *p*, cm^{-3}
348	743.4	5.1	8	$p=1.5\times10^{17}$
350	210.3	2.7	11	$p=2.2\times10^{17}$
353	100.9	1.7	15	$p=2.4\times10^{17}$
354	69.1	0.09	193	$n=3.5\times10^{17}$

superconducting magnet. The microwave resonator ($Q\sim10\,000$) was of rectangular TE_{011} form with appropriate optical access and could be rotated about an axis perpendicular to the magnetic field. The PL was excited with the UV lines either from an argon-ion laser or from a He-Cd laser, typical excitation powers being in the region of 20 mW. The entire sample surface (of area about 10 mm^2) was illuminated without focusing, giving a typical illumination intensity of 0.2 W cm^{-2}. The incident microwaves were chopped at frequencies in the range 100 Hz–100 kHz and changes in the PL intensity were monitored with an S20 response photomultiplier and a lock-in amplifier; the modulation of the PL under magnetic resonance conditions was in the range 0.1–0.01 %. The PL emitted either along or at right angles to the magnetic field could be monitored and suitable parts of the spectrum were selected through use of filters or an auxiliary spectrometer.

III. EXPERIMENTAL RESULTS

A. Photoluminescence spectra

The room-temperature PL spectra for the four samples studied are shown in Fig. 1. The spectra are typical of MOVPE-grown GaN doped with Mg[9] and show three main features,[10] the periodic structure being due to interference effects. For the room-temperature measurements, a UV microscope system with 244-nm excitation was used and a high excitation density was therefore achieved; these are not the conditions under which ODMR was investigated, but the spectra are presented here to facilitate the following comparison with nominally similar samples of other groups, since micro-PL is a very widely applied technique. The spectra of Fig. 1 are not corrected for the spectral response of the measurement system, but the main effect of this correction is a displacement of the peak positions by less than 50 meV to lower energy.

There is a relatively narrow band at approximately 3.42 eV for the samples expected to have the lowest Mg content (Samples 354 and 350). This band lies at the energy expected, on the basis of temperature-dependent reflectivity measurements,[11,12] for the feature associated with the *A* valence band and is therefore often ascribed to free exciton recombination. Second, we observe a broader band at around 3.2 eV (clearest in our spectra for sample 350). This has been tentatively attributed to the recombination of free electrons (or electrons bound to shallow donors) with neutral Mg acceptors.[10] Finally, there is a second broad band, peaking at 2.8–2.9 eV, which is referred to often as the ''blue band'' and has been observed previously to dominate the spectra of the samples having the highest Mg content.[10,13] This observation is confirmed for the present series of samples. This 2.8-eV band has been the subject of considerable discussion and is generally believed to be due to recombination between deeper donors and shallow acceptors such as Mg,[8,10,14–16] though the alternative mechanism of recombination between a conduction band electron and a deep Mg-related center has also been proposed.[17,18] Recently, it has been suggested that the blue emission band may have different origins in heavily and in weakly doped GaN; Fig. 1 shows the PL spectra of

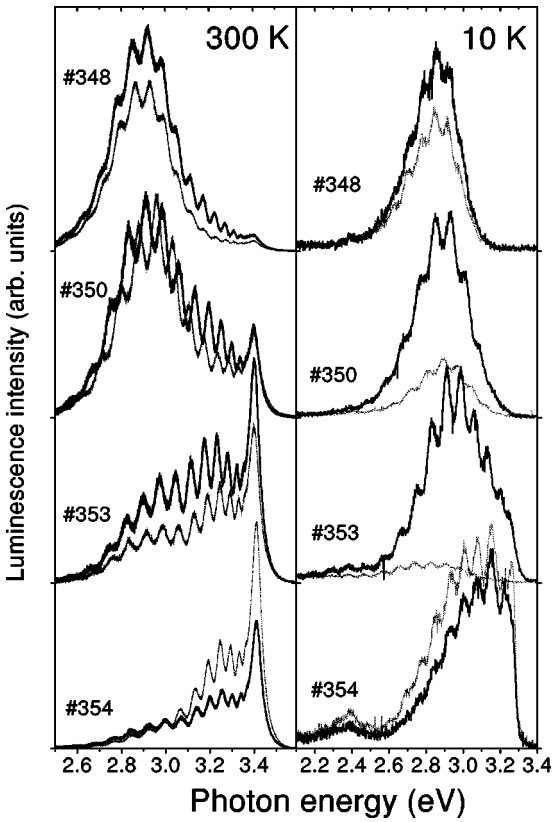

FIG. 1. Left: room-temperature photoluminescence spectra of the four GaN:Mg samples in decreasing order of Mg content from top to bottom. The spectra are displaced vertically for clarity and their baselines are indicated by the ticks; for each sample, the heavier and lighter traces show the PL spectrum before and after annealing, respectively. Right: the corresponding low-temperature spectra.

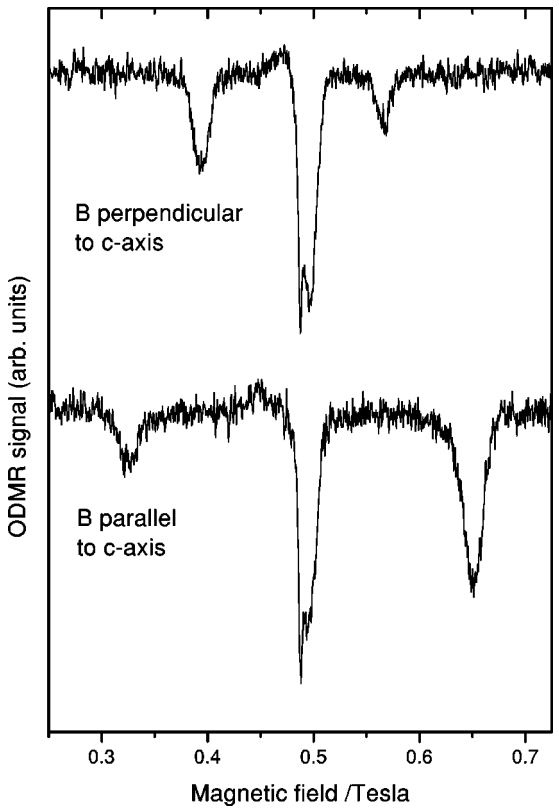

FIG. 2. ODMR signals from as-grown GaN:Mg (specimen 354) at 1.5 K with a microwave chopping frequency of 6 kHz. The signals represent decreases in PL intensity when the microwaves are on. The upper and lower traces were recorded in the Voigt and Faraday geometries, respectively.

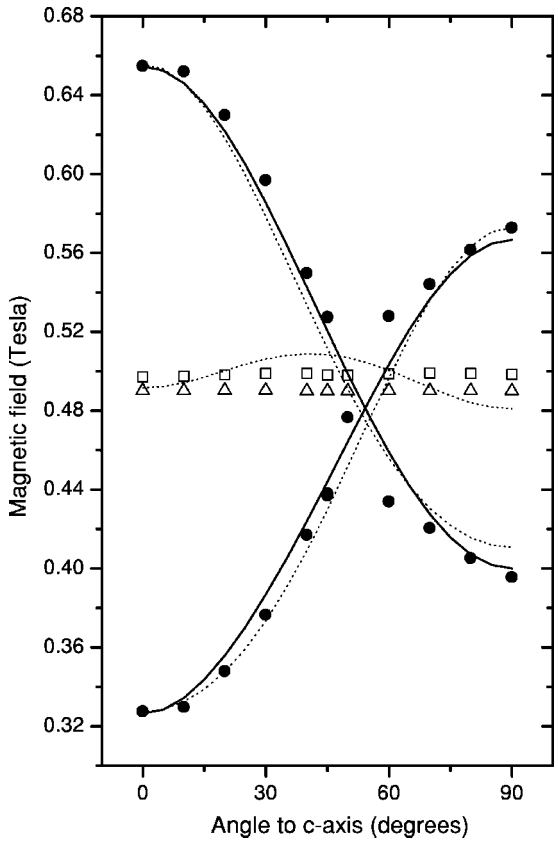

FIG. 3. The dependence on the angle between the *c* axis and the magnetic field of (i) the ODMR signals of interest in this work (solid circles) and (ii) the central ODMR lines (squares and triangles) together with simulations of the data on the basis of the model of Eq. (1) with spins of $S=1$ (solid lines) and $S=3/2$ (dotted lines).

each sample before and after annealing; we do not observe any large changes of the PL spectra on annealing, as was also noted in earlier work.[11]

At low temperatures, the PL features already described shift in accordance with the expected shift of the band gap.[12] A weak green band is now observed in sample 354, which has the lowest Mg content (see Table I). These spectra were obtained with 325-nm excitation and a conventional single-grating spectrometer with 2-Å resolution and are again uncorrected for the system response. The upper limit of the energy range of the PL detected in the ODMR experiments was 3.2 eV and the lower energy limit could be chosen so as to include only the blue band or both the green and blue bands.

B. ODMR spectra in as-grown material

The ODMR spectra described in the present paper were obtained by monitoring the blue emission (Fig. 1, right) and were observed as luminescence decreasing signals (monitoring in the green region also reveals the same signals but this may well be due to the low-energy tail of the blue band). Typical spectra are shown in Fig. 2, for directions of the magnetic field along and perpendicular to the *c* axis and for a microwave chopping frequency of 6 kHz.

The positions of the two outer signals are strongly dependent on the direction of the magnetic field **B**, as shown in Fig. 3, whereas the signals at the center of the spectra are isotropic. The pattern shown in Fig. 3 was found to be independent of the plane in which the magnetic field was oriented, provided that it contained the *c* axis. The anisotropic signals were thus shown to possess axial symmetry relative to the *c* axis, so that the appropriate spin Hamiltonian is

$$H=g_{\parallel}\mu_B B_z S_z+g_{\perp}\mu_B(S_x B_x+S_y B_y)+D\left(S_z^2-\frac{1}{3}S(S+1)\right), \tag{1}$$

where the *z* direction is along the *c* axis and where μ_B is the Bohr magneton.

We have fitted the spectra with a spin $S=1$, as shown by the solid lines in Fig. 3, with the parameters $g_{\parallel}=2.00\pm0.02$, $g_{\perp}=2.00\pm0.02$, $|D|=4.52\pm0.12$ GHz. We also considered the possibility that $S=3/2$, but were unable to obtain a satisfactory fit: in Fig. 3, we show (by the broken line) the behavior expected if $S=3/2$ for the parameters $g_{\parallel}=2.00$, $g_{\perp}=2.00$, $|D|=2.26$ GHz and it is clear that the fit to the signals near 0.5 T is unsatisfactory: not only is there a predicted, and unobserved, anisotropy but also the field positions of the central signals when along or perpendicular to the *c* axis are predicted to be lower than observed. We therefore exclude the possibility that $S=3/2$ and ascribe the

central lines to centers that are different from that which produces the two outer signals. Confirmation of this conclusion is provided by the slightly different behavior of the outer signals and the inner ones when the microwave chopping frequency is altered. We also exclude the possibility that the spin S is greater than 3/2 since there is no evidence of the additional signals that would then be expected.

The sign of the zero-field splitting parameter D remains undetermined. At first sight, the relative intensities of the transitions at 0.65 and 0.32 T in the 0° spectrum in Fig. 2 (bottom trace) suggest that D is positive, since in a conventional ESR experiment a thermalized population at 1.8 K would lead to the lower field transition being weaker than the one at the upper field by a factor of 1.5. However, for the ratio of intensities to equal the observed value of 4, the temperature would have to be as low as 0.2 K. We conclude therefore that the ratio of the line intensities is not determined by simple thermalization considerations and therefore does not give the sign of D.

When the signals due to the $S=1$ spectrum have been taken into account, there remain the isotropic lines near 0.5 T. These are both fitted by effective spins of 1/2, with values of $g_{\|}=g_{\perp}=2.007\pm0.005$ for the narrow line [full width at half maximum (FWHM) 5 mT] and $g_{\|}=g_{\perp}=1.974\pm0.005$ for the broad line (FWHM 11 mT). The g value and width of the broader of the $S=1/2$ lines correspond closely those of a center observed by Ref. 19 in semi-insulating GaN and attributed to a deep donor. The sharper line has a width similar to that of a signal reported in Zn-doped GaN, though its g value is slightly higher than the 1.997 reported in that case. It is worth noting that we observe the sharper line most easily in magnesium-doped GaN and that it is very weak in zinc-doped GaN that we have studied; furthermore, we observe the sharp line in a GaN:Mg sample grown without an underlying zinc-doped layer such as that present in the samples discussed here. The g value of the sharp line is in fact close to the value of 2.003 reported for Mg-doped films and attributed to deep donors,[8] though the present linewidth of 5 mT is less than that of Ref. 8 (15–20 mT). When monitoring exclusively the green region, some additional ODMR signals are observed which will be described elsewhere.

C. Effect of magnesium concentration on the ODMR spectra

When the magnesium concentration in the specimens is increased, there are marked changes in the ODMR spectra, as shown in Fig. 4. The $S=1$ spectrum becomes weaker (Fig. 4 sample 353) and then disappears (Fig. 4 samples 350 and 348), while in the central region the luminescence-quenching signals are replaced by luminescence-enhancing signals with different g values (Fig. 4 samples 350 and 348). The stronger of the signals in Fig. 4 (348) has an isotropic g value of 1.96 ± 0.01 and a FWHM of 25 mT and is very similar to a signal already observed in GaN:Mg and attributed to electrons trapped at donors.[7] The weaker signal has a value of $g_{\|}=2.09\pm0.01$ (field along the c axis) and FWHM of 18 mT; when the field is rotated away from the c axis, this line moves towards a g value of 2.00 and is therefore very similar to the Mg-related signal reported by several workers[19] and recently attributed to shallow Mg acceptors.[8] The details of the spectra in the central region are sensitive to the value of the microwave chopping frequency. As an example, the effect on the spectrum in Fig. 4 (350) of reducing this frequency from 6 kHz to 600 Hz is shown by the dotted line; under these conditions, the sharp luminescence-quenching signal re-appears.

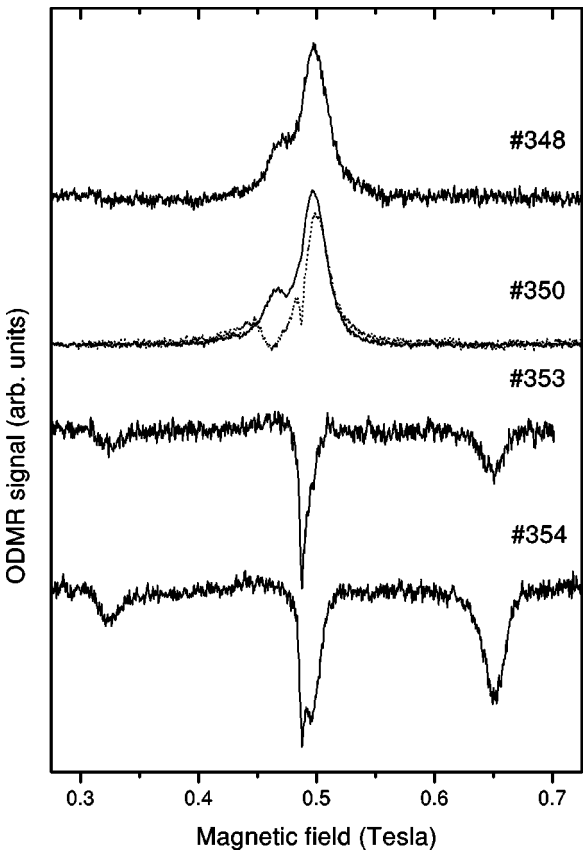

FIG. 4. ODMR signals from the four GaN:Mg samples in order of decreasing magnesium concentration from top to bottom. The microwave chopping frequency is 6 kHz (solid lines). A reduction of the chopping frequency to 600 Hz leads to changes of the ODMR spectrum of the 350-as grown sample (dotted line).

The complicated dynamic behavior of the ODMR response is also illustrated by the dependence of the spectra on the laser power. The $S=1$ signals are best observed at the high laser intensities normally used (0.2 $\mathrm{W\,cm^{-2}}$). In the case of specimen 354, reducing the illumination intensity to about 2 $\mathrm{mW\,cm^{-2}}$ causes the $S=1$ signals to disappear and to be replaced by weak luminescence-enhancing signals similar to those in Fig. 4 (348).

D. Effects of annealing on the ODMR spectra

Annealing for 10–15 min at 800 °C in nitrogen at atmospheric pressure leads to disappearance of the triplet state spectra and the spectra then have the appearance of that in Fig. 4 (348), though they are considerably weaker. The disappearance of the $S=1$ ODMR signals correlates with the changes in the PL spectra on annealing which are shown in Fig. 1.

IV. INTERPRETATION OF THE $S=1$ SPECTRA

There have been several reports of triplet state ODMR spectra in GaN, some in irradiated structures and some in doped material. However, none of the previously reported spectra have the same spin-Hamiltonian parameters as those observed here. Two possible situations need to be considered. One is that the triplet state is formed as the result of exchange coupling between two spins located at spatially separate sites that are sufficiently close for there to be a measurable magnetic dipole-dipole interaction between them. The second possibility is that two unpaired electrons are trapped at the same site (e.g., two electrons trapped at a nitrogen vacancy) and that the exchange interaction between them favors the triplet configuration. We consider the two cases in turn.

A. Interpretation as a pair spectrum

The simplest form of spin-exchange coupling between two spins $\mathbf{s}_1$ and $\mathbf{s}_2$ each of 1/2 can be represented by an isotropic interaction of the form $a\mathbf{s}_1\cdot\mathbf{s}_2$. It is well known[20] that if the exchange parameter $a \gg |(g_1-g_2)\mu_B B|$, where g_1 and g_2 are the g values of the spins, a triplet state is formed that can be described by the spin-Hamiltonian of Eq. (1), with a g value given by the mean of the two interacting spins and with a zero-field splitting parameter D which contains contributions due to anisotropic exchange and due to the magnetic dipole-dipole interaction. If the g values are isotropic (so that spin-orbit admixtures to the ground state are insignificant), the exchange contributions to D are expected to be small and D will be given by the dipole-dipole expression $D=-(\mu_0/4\pi)(3g_1g_2\mu_B^2/2r^3)$, where r is the distance between the spins. An example of such a situation is provided by the ESR experiments on coupled holes at adjacent oxygen sites in ZnO,[21] and, recently, by studies of Frenkel pairs in electron-irradiated GaN.[22] In the present case, if it is assumed that $g_1 \approx g_2 \approx 2$, the value of $|D|=4.4$ GHz corresponds to $r \approx 0.26$ nm, so that the two spins would be separated along the direction of the c axis by a distance of this order. Care should be exercised in taking the value of 0.26 nm as an accurate figure, since the dipole-dipole formula can be only a first approximation to the zero-field splitting parameter. Nevertheless, to put the figure in context, we note that, in GaN, the value of the parameter c is 0.52 nm, the bond length in the c direction is 0.20 nm and the anion-cation separation in the c direction across the octahedral cage is 0.32 nm.

We note further that the ODMR spectra show no evidence of hyperfine splitting, which suggests that, whatever the nature of the participating centers, they are not such that there is a strong localization of the wave function on a particular gallium, nitrogen (or indeed, hydrogen) atom, since each of these elements have naturally occurring isotopes that predominantly have finite nuclear spins. The participating centers would thus have to involve elements whose naturally occurring isotopes are predominantly those with nuclei of zero spin (such as magnesium, oxygen, silicon, or carbon), or the wave functions would need to be such that their density was small at any magnetic nucleus.

We consider the following possibilities for the relative positions of the spins, in each case with the axis joining them being in the c direction: (i) they are located at adjacent octahedral interstitial sites, the separation being $c/2 = 0.26$ nm; (ii) they are located at adjacent bonding sites, nominally separated by 0.20 nm; (iii) they are located at opposite sides of the octahedral cage, nominally separated by 0.32 nm; (iii) they are located at a substitutional site paired with a tetrahedral interstitial site (nominal separation 0.36 nm).

The octahedral-octahedral interstitial model has the immediate advantage that the intrapair separation corresponds to that given by the dipole-dipole formula. Oxygen is a common impurity in GaN (Ref. 23) [we estimate from secondary-ion mass spectrometry (SIMS) data that in our specimens the oxygen concentration is typically 10^{16} cm^{-3}] and an oxygen interstitial/magnesium interstitial is therefore a possible candidate, with the oxygen attracting a hole and the magnesium an electron. The g values of the individual centers would be expected to be close to 2.0, leading to the correct g value for the pair (an electron trapped on the magnesium ion would be in essentially an s-type orbit and would be expected to have a g value close to 2; the g values for a hole trapped on the oxygen atom are more difficult to predict, but studies of holes trapped on oxygen ions in, e.g., ZnO,[21] suggest that the g values would be in the range 2.00–2.02). Thus an interstitial magnesium/interstitial oxygen model would be consistent with all the spin-Hamiltonian parameters.

An alternative model involving oxygen and magnesium is that they lie respectively at nitrogen and gallium substitutional sites, rather than interstitial locations. As noted above, there are two possibilities, each with the Mg-O axis along the c direction. The first is that the two elements lie at adjacent bonding sites and the second that they lie at opposite corners of the octahedral cage. The nominal distances between the cation and anion sites would, respectively, be 0.20 and 0.32 nm, so there would need to be significant relaxation if the simple dipole-dipole expression were to be valid and to give the observed value of D. Individually the magnesium and the oxygen are expected to act as acceptors (A) and donors (D), so that the complex could in principle form the state $A^+ - D^-$. It has been suggested by Tripathy *et al.*[24] that such complexes can form near the GaN surface following treatment in KOH and molecular doping by MgO has been tentatively proposed by Pankove *et al.*[25] Recent studies[23] of the electrical activity of GaN:Mg have also shown that oxygen donors and magnesium-containing complexes (which dissociate above 600 °C) have a strong influence on the conductivity.

If the pair model is the correct one, one would expect the g value of the triplet state to be given by $(g_A+g_D)/2$, where g_A and g_D are the individual g values for the acceptor and donor species. For donor centers in GaN, the g-values for center of mass donors are in the region of 1.95 while for deeper donors they are typically in the range of 1.96–2.00,[7] according to the depth. Experimentally, the g value for the triplet state is isotropic at 2.00 ± 0.02 and it is difficult to see how this can be achieved if shallow donors are involved.

This suggests that one member of the pair is a deep donor (for example, substitutional oxygen). If we assume that the g value of such donors is essentially isotropic at 2.00, the second member of the pair must also have an isotropic g value, that is both $g_{\parallel}$ and $g_{\perp}$ must lie in the range 2.00 ± 0.04 (so that the triplet state has $g_{\parallel}$ and $g_{\perp}$ in the experimentally determined range 2.00 ± 0.02).

For acceptors, recent studies[8] suggest that the Mg acceptor g values are anisotropic, with values for $g_{\parallel}$ ranging between 2.11 and 2.06, with $g_{\perp}$ between 1.97 and 2.01. These variations are attributed to different states of strain in the various specimens studied. If the present triplet state spectrum is due to a pair formed by a deep donor coupled to an acceptor, the value of $g_{\parallel}$ for the acceptor must be less than 2.04. This lies outside the range attributed to isolated Mg acceptors[8] (though it is possible that the presence of the nearby deep donor causes a sufficient perturbation of the local environment for the the g value to shift in this way).

A further possible model is one in which the magnesium is paired, not with a substitutional oxygen, but with a nitrogen vacancy, the latter acting as a deep donor (as has been predicted theoretically). Such a model would be difficult to distinguish from one involving the oxygen donor, but would also suffer from the problem posed by the value of $g_{\parallel}$. Yet another possibility involving paired centers is a complex formed from substitutional magnesium and tetrahedral interstitial magnesium ions, the latter acting as a deep donors. Again, this also suffers from the problem with $g_{\parallel}$.

A further difficulty with any of the models in which one of the components of the pair is a substitutional ion is that, as already noted, the local distortions would have to be very large in order to change the pair separation from 0.20 nm (or 0.32 or 0.36 nm) to the value of 0.26 nm deduced from experiment. Typically, total-energy calculations predict changes in bond lengths of only a few percent, so such a relaxation appears unlikely. If a substitutional ion is indeed involved, the dipole-dipole expression for D must be breaking down.

The discussion above has focused on models in which the magnesium is paired with oxygen. Instead of oxygen, we need also to examine the possibility that the second impurity is silicon or carbon. Silicon is a common impurity in GaN and from SIMS measurement is present at a typical level of 10^{16} cm^{-3}, being believed to act as a donor, substituting at a gallium site (see, e.g., Ref. 26 and references within). This implies that a substitutional-magnesium/substitutional-silicon pair would not be aligned along the c axis and is thus not a candidate for the observed spectrum. In contrast, an interstitial-magnesium/interstitial-silicon pair would have the correct symmetry; however, although we cannot exclude such a model, it seems less favorable than a magnesium-oxygen pair unless the silicon, like the oxygen, were to be doubly negatively charged. In the case of carbon, SIMS data shows that this element is present at a level of 10^{17} cm^{-3}. Carbon is believed to substitute at nitrogen sites and to act as an acceptor.[27] However, although models involving substitutional carbon can lead to the correct symmetry they suffer, like other substitutional models, from the need for significant local distortion to account for the value of D. Further, a model involving paired acceptors does not seem likely. An interstitial-magnesium/interstial-carbon model cannot be excluded, but suffers from the same disadvantage as one involving silicon.

To summarize, the model which best fits the spin-Hamiltonian parameters appears to be the interstitial magnesium/interstitial oxygen model, though the other possibilities cannot definitely be excluded. Though the formation energy of isolated interstitials may be high, it may be reduced in the case of paired interstitials because of the Coulomb interaction. We are not aware of any calculations for the formation energy of the complex we propose in wurtzite GaN; however, *ab initio* calculations for cubic GaN suggest that a substitutional Mg-O pair is stable.[28]

The mechanism by which ESR in the complex leads to luminescence-quenching ODMR signals is complicated and, like other mechanisms by which $S=1$ ODMR signals are observed in GaN, is not fully understood. If magnesium-oxygen pairs are indeed involved, the disappearance of the $S=1$ signals in the more highly Mg-doped specimens may be a consequence of the limited amount of oxygen present in the material and the resulting decrease in the relative importance of the triplet states in the dynamical processes that lead to the ODMR signals. The disappearance of the signals on annealing may be a result of changes in the structure or charge state of the pair center or, again, be due to a reduction of its influence on the dynamical processes.

B. Interpretation as a two-electron center

A completely different possibility is that the triplet state is formed by two electrons trapped at the same site. The most obvious candidate is a nitrogen vacancy V_{N}, since such vacancies are predicted to be formed easily in p-type material.[29] Evidence from wide-gap alkaline-earth oxides (e.g., CaO) suggests that two electrons trapped in a negative-ion vacancy can form excited triplet states,[30] with values of the zero-field splitting parameter D typically in the region of (though somewhat smaller than) the value observed in the present spectra. The g values of such spectra are usually very close to 2.00, as observed here. The dipole-dipole expression for D is not relevant when the two electrons are at the same site, and the fact the expression leads to a separation distance of 0.26 nm would then be purely accidental. The form of the spin-Hamiltonian [Eq. (1)] would arise directly from the overall wurtzite symmetry of the crystal.

However, in the case of GaN, first-principles calculations of the ground-state electronic structure of the V_{N} center suggest that it consists of a spin singlet $S=0$ resonant with the valence band and a p-like state resonant with the conduction band.[29] Thus the only *ground*-state configuration of the center possessing a nonzero spin is the V_{N}^{2+} state with spin $S=1/2$.[31] If a nitrogen vacancy were to participate in ODMR and to give rise to the $S=1$ signal we observe, it would therefore have to be in the charge state V_{N}^{1+} (in order to possess two electrons) but in an excited, triplet state. It is not presently known whether such a state is bound but, even if it were, it is not clear how ESR in this excited state could give rise to a modulation of the PL intensity. In the case of F

center ODMR in CaO, in which a triplet excited state is known to be involved, the PL that is monitored is that emitted on relaxation of a doubly occupied vacancy from its triplet to its singlet state and both luminescence-enhancing and luminescence-quenching signals are observed (according to the polarization).[30] In our case, there is compelling evidence (from the identification of the PL spectra of Fig. 1) to suppose that the emission that we observe in GaN:Mg arises from a donor-acceptor pair recombination and not from transitions between different vacancy configurations. In addition, the signal that we observe is always luminescence quenching. We therefore believe that the interpretation of the signals in terms of a two-electron center may be discounted.

V. CONCLUSIONS

A previously unreported triplet state ODMR spectrum has been observed in GaN:Mg. The signals are ascribed to a spin of 1 complex formed by two exchange-coupled spins of 1/2. The magnitude of the zero-field splitting parameter D corresponds to a separation between the individual members of the pair of 0.26 nm and the axial symmetry corresponds to alignment of the pair along the c axis. A model which gives good agreement with the observed g values and with the zero-field splitting parameter is one in which magnesium and oxygen ions lie at adjacent octahedral interstitial sites. In contrast, models involving substitutional magnesium acceptors are problematic, since, if a recent attribution[8] of ODMR signals near $g=2$ to such acceptors is correct, it becomes difficult to reconcile the predicted and observed g values for the triplet complex. A further difficulty with models involving substitutional ions is that the dipole-dipole formula, if valid, predicts an intrapair separation that would involve large local distortions. The present result therefore best accounted for by the magnesium interstitial/oxygen interstitial model: the formation of such a complex would be of direct relevance to the compensation processes that occur during the growth process in this material.

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*Electronic address: d.wolverson@bath.ac.uk; URL: http://staff.bath.ac.uk/pysdw

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