# Nature of acceptor states in magnesium-doped gallium nitride

G. N. Aliev, S. Zeng, J. J. Davies,* D. Wolverson, and S. J. Bingham
*Department of Physics, University of Bath, Bath, BA2 7AY, United Kingdom*

P. J. Parbrook and T. Wang
*Department of Electronic Engineering, University of Sheffield, Sheffield, United Kingdom*
(Received 22 December 2004; revised manuscript received 28 February 2005; published 25 May 2005)

The most effective method of producing *p*-type gallium nitride is currently through incorporation of magnesium. However, such doping leads not only to the desired shallow acceptors but also to the creation of much deeper energy levels. Magnesium-related acceptors have been observed in many optically detected magnetic resonance experiments and their magnetic properties, as characterized by the *g* values of the holes which they trap, have been found to vary significantly according to the growth conditions and doping levels. The purpose of the present paper is to present a model that accounts for these observations. The model assumes that, in the deep acceptors, the hole is located in an atomic orbital of *p* character, presumed to be on a nitrogen atom. The orbital degeneracy is partly removed by the wurtzite crystal field and finally by a reduction in local symmetry associated with the relative positions of the magnesium dopant and the nitrogen atom upon which the hole is localized. Further changes in the local crystal field are caused by the presence of nearby defects or by strain. These changes in the crystal field are accompanied by changes in acceptor depth. The approach leads to the correct *g* values and the correct correlation between the *g* values and acceptor depth for reasonable choices of the parameters. In the limit that the low symmetry fields become small, the model evolves to one that is consistent with the correct forms of the ground and near-ground Kramers doublets that are observed by other workers in studies of shallow acceptors in material that is not doped with magnesium. Finally, the model is shown to be entirely consistent with a range of acceptor states of different depths being formed by simple substitution of a magnesium ion at a gallium site, rather than by the creation of more complicated defects. The conclusion also highlights the need for the GaN to be of high crystalline quality if effective *p*-type doping is to be achieved.

DOI: 10.1103/PhysRevB.71.195204 PACS number(s): 71.55.Eq, 71.70.Fk, 76.70.Hb, 78.55.Cr

## I. INTRODUCTION

There is at present considerable interest in the nature of acceptor states in GaN and related materials, driven by the need to optimize *p*-type doping for device applications. To date, the most successful *p*-type dopant is magnesium, but the effectiveness of such doping is limited by the fact that only a minor fraction of this element appears to be incorporated as simple acceptors. Furthermore, in layers produced by metal-organic vapor phase epitaxy (MOVPE), it is necessary to anneal the material before the acceptors are activated. The implication is that much of the incorporated magnesium does not simply substitute for gallium but that it is often associated with, or perturbed by, other impurities or defects, or, alternatively, that it can lie at other sites. To obtain a clearer understanding of the behavior, several high resolution spectroscopic techniques have been employed, prominent amongst which have been optically detected magnetic resonance (ODMR) and photoluminescence (PL) in the presence of magnetic fields. From ODMR studies, considerable information[1–5] has been obtained for magnesium-related acceptorlike states and a number of models have been proposed[1–6] for the luminescence processes associated with magnesium doping (Ref. 5 contains a useful summary). More recently, ODMR experiments on homoepitaxial GaN:Si have led to the observation of acceptors consistent with effective mass behavior,[7] but whose chemical identity remained unidentified. The magneto-optical behavior of acceptors is strongly influenced by the *local* crystal fields in which they reside and by the coupling between the spin and orbital angular momenta of the trapped hole and a recent PL study[8] of undoped homoepitaxial GaN in high magnetic fields suggested the existence of an acceptor state in which the spin-orbit coupling was strongly quenched. The present ODMR study, which concerns the deep acceptor states in magnesium-doped epitaxial layers of GaN, is aimed at clarifying what appears to be a complicated situation and was motivated by the observation of systematic changes in the magnetic properties of the acceptorlike states in individual specimens as a function of their position in the forbidden gap.

The plan of the paper is as follows. First we outline the ODMR technique and the experimental data. We then present a model (which differs from one put forward earlier[9]) that accounts for the magnetic parameters of the deep acceptors and their systematic behavior. The relationship between deep acceptors and those that are shallow is then discussed.

## II. EXPERIMENTAL DETAILS

### A. The ODMR technique

ODMR has long been used for the investigation of recombination emission in semiconductors, in particular for studies of recombination of an electron from a neutral donor with a hole from a neutral acceptor. The technique relies on the fact

 

that there are spin-selection rules in the recombination process, so that changes in the spin distribution of either the donor or of the acceptor lead to changes in the polarization or intensity of the PL. Such changes in spin distribution are caused when magnetic resonance transitions are induced between the Zeeman components (spin up, spin down) of the donor and acceptor states. Hence, by monitoring the PL, magnetic resonance spectra of the donor and acceptor states can be obtained. Discussions of the technique and of the mechanisms by which signals are observed are given in Ref. 10. The ODMR spectra are sensitive not only to the donors and acceptors directly involved in the recombination process that is being monitored, but also to centers involved in recombination mechanisms that are in competition with the PL process, so that caution has to be taken in interpretation of data. In the present study, the specimens were mounted in a $TE_{011}$ 14 GHz rectangular microwave cavity with suitable optical access. The unloaded cavity $Q$ was of the order of 3000 and the incident microwave power was about 50 mW. The specimens were in direct contact with liquid helium at 2 K and the PL was excited by the UV lines from an argon ion laser (363.8 and 351.1 nm, 3.41 eV and 3.53 eV, incident power density $\sim 1\ \mathrm{mW\,mm^{-2}}$). Different wavelength ranges of the PL were selected with transmission filters, each with a pass band of 50 nm, and changes in intensity that occurred as the microwave power was switched on and off were recorded with a lock-in system as the magnetic field was swept slowly. The microwave assembly could be turned about a vertical axis, so that the angle between the *c* axis of the specimen and the horizontal magnetic field in the superconducting magnet could be varied between 0° and 90°. PL spectra were recorded under excitation from the UV line (325.0 nm, 3.81 eV) of a He-Cd laser.

### B. Details of the specimens

The samples were grown on *c*-plane sapphire substrates in a Thomas-Swann close-coupled showerhead reactor operating at low pressure. The magnesium-doped layers were of thickness 1.5 $\mu$m and were grown at a temperature of 1047 °C directly onto a thin nucleation layer of GaN grown at 525 °C. The magnesium precursor flow rates were 75, 100, 200, and 300 standard cubic centimeters per minute (samples 626, 625, 624, and 623, respectively), producing a range of magnesium concentrations, which were not determined directly but are expected to increase monotonically with the precursor flow rate. One layer (621) was undoped. The specimens were annealed in nitrogen at atmospheric pressure at 850 °C for 20 min.

### C. The PL spectra

A typical PL spectrum is shown in Fig. 1(c). There are weak excitonic features in the region around 3.5 eV that are not of direct interest in the present context. In common with previous workers,[1] we ascribe the broad emission band extending from 3.1 to 2.5 eV to recombination between donors and acceptors. This attribution is supported by the ODMR results described below.

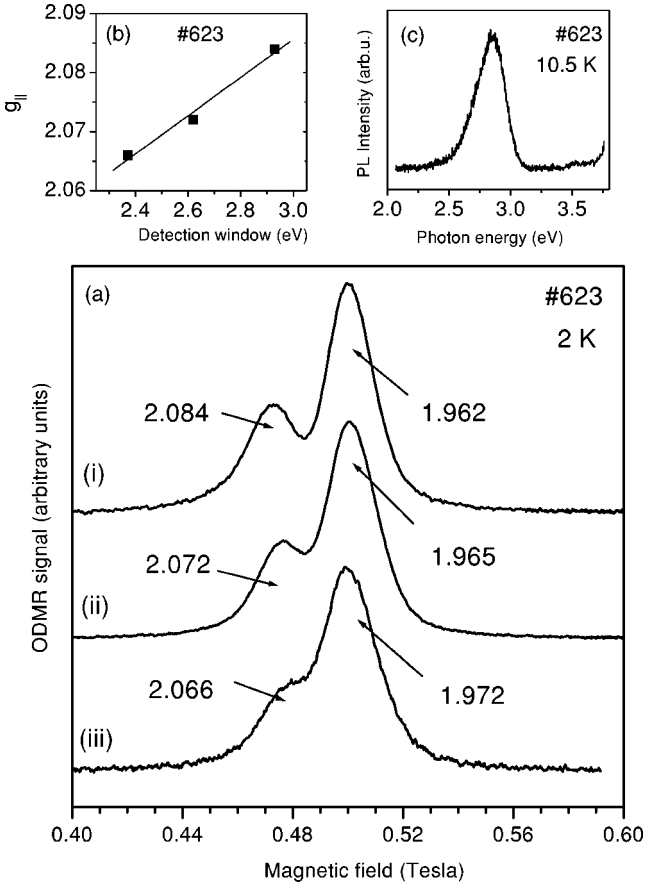


FIG. 1. (a) The ODMR spectra for specimen 623 with detection at different PL energy ranges: (*i*) 2.75 to 3.1 eV; (*ii*) 2.48 to 2.75 eV; (*iii*) 2.25 to 2.48 eV. The microwave frequency was 13.76 GHz and the temperature was 2 K. The magnetic field was along the crystal *c* axis. (b) The values of $g_{\|}$ for deep acceptors in specimen 623, measured at three different detection windows, centered at the energies shown. (c) The PL spectrum at 10 K for specimen 623 under UV excitation from a He-Cd laser.

### D. The ODMR spectra

ODMR spectra for specimen 623 for the magnetic field along the crystal *c* axis and obtained by monitoring different regions of the PL spectrum are shown in Fig. 1(a). In each case, the spectrum consists of two prominent signals, and, following previous workers,[1–5] the line at the higher magnetic field is attributed to donor centers, while that at the lower field is assigned to acceptors. Measurements at different angles show that the field values for each signal can be described by

$$h\nu = \mu_B B \sqrt{g_\perp^2 \sin^2\theta + g_\|^2 \cos^2\theta}, \tag{1}$$

where $h\nu$ is the microwave photon energy, $\mu_B$ is the Bohr magneton, and $B$ is the magnetic field, which is at an angle $\theta$ to the *c* axis (which is the growth direction). As $\theta$ is increased from zero, the acceptor signals move towards the donor signals and merge with them. The values of $g_\perp$ for the acceptors are in the region of 2.00 but, because of the overlap with the donor signals, cannot be measured accurately. The values of $g_\|$ for the acceptors are consistent with the

range reported by several authors, as are the values for the signals attributed to the donors (see Sec. III).

For each Mg-doped specimen, the values of $g_{\|}$ for the acceptors are found to depend on the detection wavelength region, showing a systematic trend in which the values of $g_{\|}$ increase as the PL detection energy $E$ increases. For specimen 623 this is shown in Fig. 1(b). As noted by previous authors,[5,11] the acceptor $g$ values also depend on the Mg concentration in a complicated manner. However, in all our Mg-doped specimens, there is a monotonic change in $g_{\|}$ with detection wavelength, with $dg_{\|}/dE$ being of order 0.040 $eV^{-1}$ in each case. Similar monotonic shifts in $g_{\|}$ with increasing detection wavelength have also been noted for GaN:Mg in Refs. 3 and 5. A wide range of $g$ values for magnesium-related acceptors has also been reported from ODMR and ESR studies,[5,11] with values of $g_{\|}$ as high as 2.10; it is important to note that, as the (positive) shifts in $g_{\|}$ become increasingly large, *negative* shifts eventually occur in $g_{\|}$ for example, when $g_{\|}=2.10$, $g_{\perp}=1.97$.[5,11]

The spectra that we discuss here are from annealed specimens. In as-grown Mg-doped layers, more complicated spectra are obtained, which are described elsewhere.[12,13] The ODMR spectra from the undoped annealed material contains only signals from donors, confirming that the signals attributed to acceptors are associated with the introduction of magnesium.

### III. ANALYSIS OF THE ACCEPTOR $g$ VALUES

We start with the premise that, since the ODMR signals are PL enhancing, the donor and acceptors that are detected are directly involved in the recombination process that is being monitored. Since the PL energies are well below the GaN band gap, one or another of the donor and acceptor levels must lie relatively deep into the forbidden gap. In electron spin resonance studies,[14] effective mass donors have been found to have $g_{\|}=1.951$ and $g_{\perp}=1.949$. In ODMR experiments, donor centers with $g_{\|}$ near 1.96 have also been reported and have been classed as "shallow;"[5] in addition, signals with $g_{\|}$ between 1.975 and 2.027 have been observed and attributed to "deep" donors.[15] The signals observed in the present study have values of $g_{\|}$ in the range 1.96 to 1.97 (see Fig. 1) and are thus attributed to "shallow" donors. It is therefore the acceptors that we take to be deep: evidence that this is correct comes from the difference in their behavior compared with that of the effective mass acceptors (depth of 220 meV) studied by Glaser *et al.*,[7] which show highly anisotropic $g$ values. The assumption is further justified by our discussion later in the paper.

If the acceptor is deep, it is reasonable to attempt to describe it in terms of well-localized wave functions (as has been done very successfully in, for example, the case of deep acceptor centers in a range of II–VI materials[16]). If, for example, the acceptor is a magnesium ion substituting at a gallium site, the hole wave function (if strongly localized) would be expected to be based on nitrogen $2p$ functions.

We begin by assuming that the holes are subject to a crystal field of purely $C_{3v}$ symmetry, together with the effects of spin-orbit coupling. The problem is similar to that analyzed some time ago by Watts *et al.*[17] when considering the case of holes located at deep phosphorus acceptors in ZnSe. The crystal field can be represented by a hole energy operator of the form $\Delta_{cfz}[l_z^2-l(l+1)/3]$ and the spin-orbit coupling by $\lambda \mathbf{l}\cdot\mathbf{s}$, where $s$ and $l$ are respectively the spin and orbital angular momenta and $\Delta_{cfz}$ and $\lambda$ are constants determined by the environment and the nature of the atoms involved ($\lambda$ is negative for holes). The states form three Kramers doublets whose splitting in the presence of a magnetic field $\mathbf{B}$ is determined by the Zeeman operator

$$H_{Zeeman} = g_s \mu_B \mathbf{B}\cdot\mathbf{s} + g_l \mu_B \mathbf{B}\cdot\mathbf{l}, \tag{2}$$

where $\mathbf{s}$ and $\mathbf{l}$ respectively represent the spin and orbital angular momentum operators, $\mu_B$ is the Bohr magneton, and where $g_l=1.00$ and $g_s=2.00$.

If the hole is localized on a single nitrogen ion adjacent to the magnesium dopant (which is assumed to lie at a gallium site), the nitrogen ion would *at first sight* need to be the one that lies along the $c$ axis in order to give the observed symmetry in the ODMR signals. One would then intuitively expect the lowest energy hole state to be of $p_z$ symmetry [Fig. 2(a)], which would correspond to a positive sign for $\Delta_{cfz}$. Provided that both $|\Delta_{cfz}|$ and $|\lambda|$ are much greater in magnitude than the Zeeman energy terms, it is their ratio $|\Delta_{cfz}/\lambda|$ that determines the way in which the $g$ values depart from the spin-only value of 2.00. The $g$ values vary with the strength of the crystal field as shown in Fig. 3. It can be seen that when the crystal field is large, the $g$ values approach the spin-only value (orbital quenching; if the crystal field were zero, the $g$ values would be isotropic at the Landé free ion value of $4/3$).

In the limit of small $\lambda$, the $g$ values can be obtained from perturbation theory. If the ordering of energy levels is as in Fig. 2, so that the hole occupies a $p_z$-like orbit, one finds

$$g_{\|} = 2.00, \tag{3}$$

$$g_{\perp} = 2.00 - 2\lambda/W, \tag{4}$$

where $\lambda$ is negative for holes and where $W=|\Delta_{cfz}|$ is positive and is the energy difference between the $p_z$ and the $p_x$, $p_y$ states. Values of $g$ consistent with these equations are observed typically for cation vacancy-associated deep acceptor centers in II–VI materials (V-centers and A-centers),[16] where the lowest energy state for a hole in a $p$ orbit is on an anion adjacent to the metal ion vacancy, the orbit being directed towards this (effectively negative) vacancy.

It is clear, however, that Eqs. (3) and (4) as they stand are not appropriate for the present case, since they predict a shift in $g_{\perp}$ rather than in $g_{\|}$. It has been suggested[9] that the discrepancy can be removed if one assumes that the hole is not localized at the nitrogen ion along the $c$ axis, but that it tunnels rapidly between all four nitrogen ions surrounding the substitutional magnesium. For any one bond, the $g$ values are such that $g_{\|B}\approx 2.00$ and $g_{\perp B}>2.00$ as in Eqs. (3) and (4), where the subscript $B$ indicates that the "parallel" axis is now along the bond direction. The delocalization is then assumed to lead to a geometrical averaging such that the effective $g$ values for directions relative to the $c$ axis are given by[9]

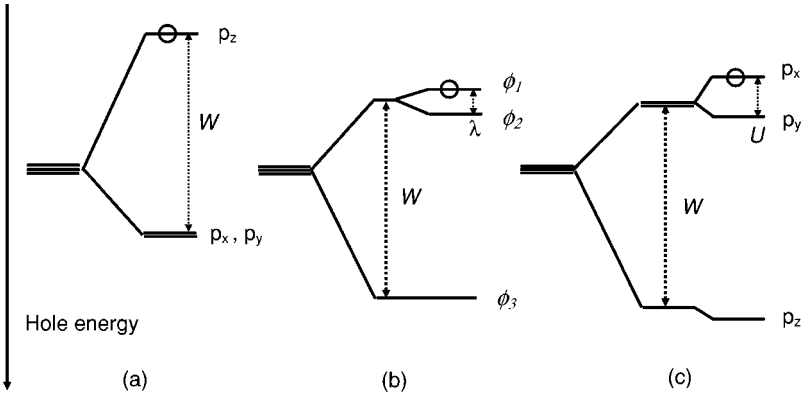


FIG. 2. The energy levels for holes in *p*-type orbits. Each level represents a Kramers doublet, which is split when a magnetic field is applied. In each case the hole occupies one of the states of the highest energy doublet. Case (a) represents a *c*-axis axial field which causes the $|p_z,1/2\rangle$, $|p_z,-1/2\rangle$ doublet to lie highest. In case (b), the sign of the *c*-axis field is reversed and the orbitally degenerate $|p_x\rangle$, $|p_y\rangle$ doublet is split by spin-orbit coupling into the doublets $\phi_1^{\pm}=|1,1/2\rangle$, $|-1,-1/2\rangle$ and $\phi_2^{\pm}=|1,-1/2\rangle$, $|-1,1/2\rangle$. The diagram is drawn for the notional case that $|\Delta_{cfz}| \gg |\lambda|$ and where $\phi_3^{\pm}$ denotes $|p_z,\pm 1/2\rangle$. Increasing spin-orbit coupling increasingly mixes $\phi_3^{\pm}$ with $\phi_2^{\mp}$. In case (c), an additional crystal field is taken to be present which removes the orbital degeneracy, the states now being of the form $|p_x,1/2\rangle$, $|p_x,-1/2\rangle$ and $|p_y,1/2\rangle$, $|p_y,-1/2\rangle$; these are mixed by spin-orbit coupling, resulting in the *g* shifts observed for the deep acceptors.

$$g_{\parallel} = [g_{\parallel B} + \sqrt{(g_{\parallel B}^2 + 8g_{\perp B}^2)}]/4 \approx 2.00 - (4\lambda/3W), \qquad (5)$$

$$g_{\perp} = [g_{\perp B} + \sqrt{(g_{\perp B}^2 + 8g_{\parallel B}^2)}]/4 \approx 2.00 - (2\lambda/3W), \qquad (6)$$

where, again, λ is negative. The approximate expressions are for small values of $|\lambda/W|$ and are indeed such that $g_{\parallel} > 2.00$, with only a smaller positive shift in $g_{\perp}$. For larger values of $|\lambda/\Delta_{cfz}| = |\lambda/W|$ these averaged *g* values are plotted as the broken lines in Fig. 3. In the range $|\lambda/\Delta_{cfz}| \ll 1$ (which is appropriate for the model of Alves *et al.*[9]) the "averaged" value of $g_{\perp}$ is greater than 2.00 [see Fig. 3 for $\log(\Delta_{cfz}/\lambda) > 1$], which is in contradiction to the experimental observations in Refs. 5 and 11. In the region that the "averaged" $g_{\perp}$ becomes less than 2.00, the predicted value of the averaged $g_{\parallel}$ would be in excess of 2.2, again not in agreement with experiment.[5,11]

We wish, therefore, to put forward an alternative model, which we shall show provides a satisfactory account of a wide range of data. In this model, we simply reverse the sign of the crystal field experienced by the hole in the direction of the *c* axis, so that an orbital doublet now lies lowest ($\Delta_{cfz}$ negative). This doublet will become further split, either by spin-orbit coupling [as in Fig. 2(b)] or by a crystal field of lower symmetry [as in Fig. 2(c)]. A field of symmetry lower than $C_{3v}$ would exist if, for example, the hole were localized not on the nitrogen atom on the *c* axis relative to the magnesium dopant, but on one of the three other nitrogen atoms that surround the magnesium. The additional crystal field that causes the reduction in symmetry is taken to be of the form $\Delta_{cfx}[l_x^2 - l(l+1)/3]$. Even further reductions in symmetry from $C_{3v}$ could be caused by the presence of strain or by a nearby second defect, leading to a variation in the quantity $\Delta_{cfz}$ (as well as in $\Delta_{cfz}$). The behavior of the *g* values over a range of values of $\Delta_{cfz}$ is shown in Fig. 4, where it is seen that there is now a positive shift in the *g* value for the magnetic field along the *c* axis ($g_z$, to be identified with the experimentally observed $g_{\parallel}$) and negative shifts when the

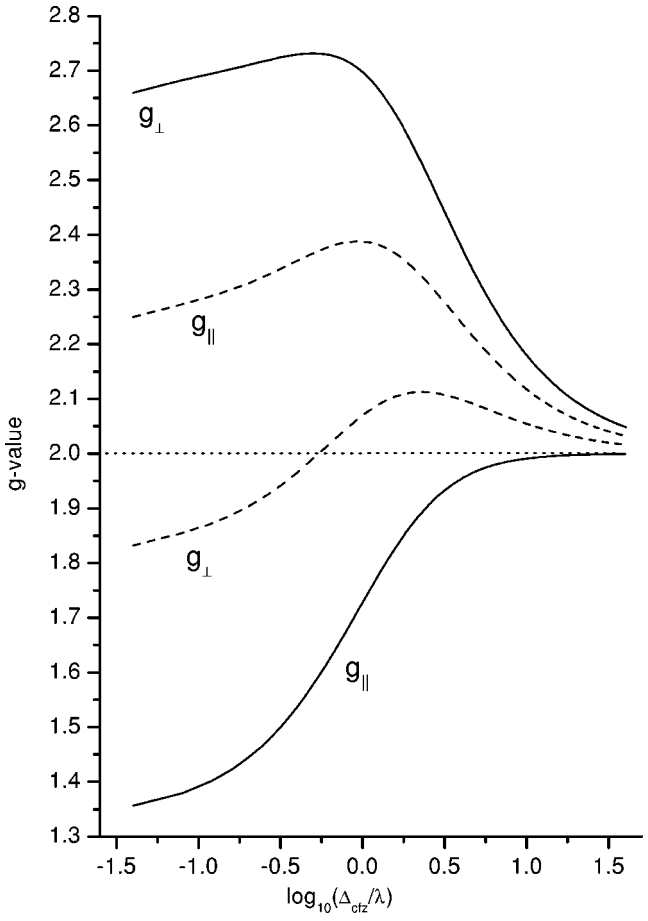


FIG. 3. The *g* values for holes at deep acceptors as a function of an axial field in the direction of the *c* axis ($U=|\Delta_{cfz}|$). For large values of the crystal field (extreme right side of the diagram), the *g* values are approximated by the perturbation expressions given in the text [Eqs. (3) and (4)]. The broken lines show calculated values according to the exact parts of Eqs. (5) and (6).

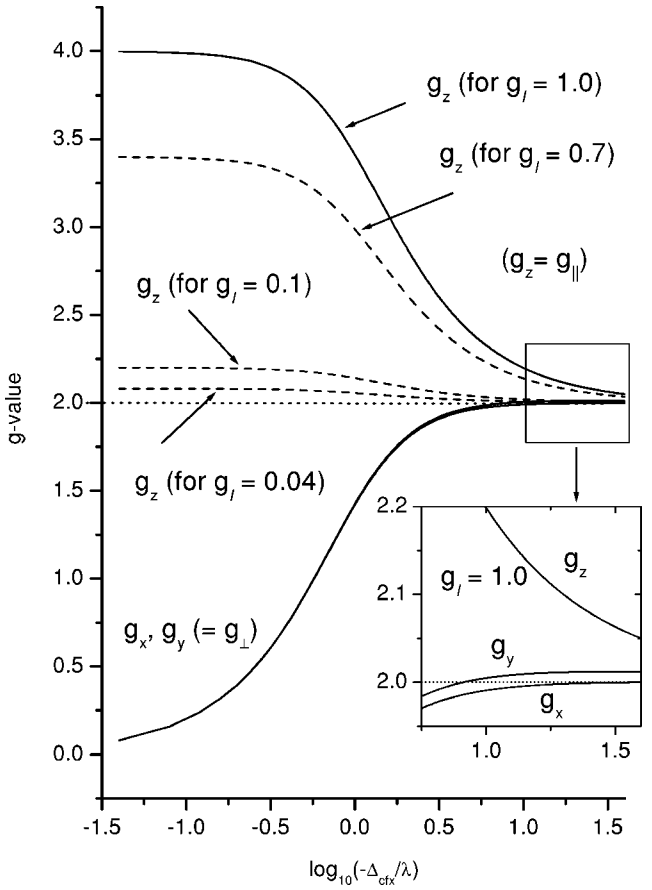


FIG. 4. The $g$ values for holes at deep acceptors as a function of an additional axial crystal field in the $x$ direction. The $c$-axis field is fixed ($\Delta_{cfz}=-1800$ meV, $\lambda=-15$ meV). If the $c$-axis field is strong, as assumed here, the components $g_x$ and $g_y$ are identical. For large values of the crystal fields, the behavior is shown in expanded form in the inset, for the case where $g_l=1.0$. In this range (extreme right of the diagram), the behavior is approximated by the perturbation expressions given in the text [Eqs. (7)–(9)]. The broken lines show the calculations for reduced values of the orbital $g$ value.

magnetic field is at a right-angle to this axis. In the calculation, $\Delta_{cfz}$ has been taken to be much smaller than $\Delta_{cfz}$, which causes $g_x$ and $g_y$ to be approximately equal (and hence identifiable with the experimentally observed $g_\perp$). The $g$ values are not sensitive to $|\Delta_{cfz}|$ provided that it is much greater than $|\Delta_{cfx}|$.

If the magnitude of $\Delta_{cfz}$ is small compared with that of $\lambda$, the $g$ values become highly anisotropic ($g_\parallel=4, g_\perp=0$) in the limit of vanishing $\Delta_{cfx}$. If, in contrast, the low symmetry field is large and splits the states as in Fig. 2(c), the $g$ values become (when $|\Delta_{cfz}| \gg |\Delta_{cfx}| \gg |\lambda|$)

$$g_x = 2.00, \tag{7}$$

$$g_y = 2.00 - 2\lambda/(W+U) \approx 2.00, \tag{8}$$

$$g_z = 2.00 - 2\lambda/U, \tag{9}$$

where $U=|\Delta_{cfx}|$. The $g$ values thus become similar to those observed for the acceptor centers in the present work ($g_z$ being identified with $g_\parallel$ and $g_x$ and $g_y$ with $g_\perp$). The value of $g_z$ is particularly sensitive to the size of the nonaxial part of the crystal field.

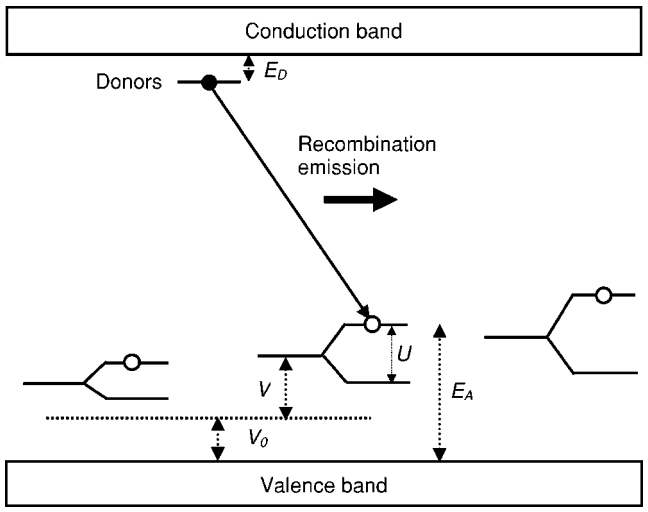


FIG. 5. The recombination processes leading to the different parts of the broad PL band. As the perturbation of the acceptor by nearby defects is increased, the $p_x$ and $p_y$ states move further into the gap and their splitting increases.

For the elements likely to lead to acceptor centers, the value of $\lambda$. is likely to be of order $-15$ meV,[18] so that a shift in $g_z$ of 0.07 (appropriate for detection centered 2.65 eV) gives $U=14|\lambda|=0.2$ eV. For the approximation $g_x=g_y$ to be reasonable, one requires $|\Delta_{cfz}|$ to be about five times $|\Delta_{cfx}|$ or more. When $g_x=g_y$ it is important to note that the actual symmetry of the acceptor (which is lower than $C_{3v}$) is not revealed by the ODMR spectra.

The sensitivity of the acceptor $g$ values to low symmetry crystal fields has been noted in a general sense by other workers[19,20] and it is of interest to attempt to use the present specific model in a quantitative manner by calculating the expected dependence of $g_\parallel$ ($=g_z$) on the acceptor depth and relating it to the dependence on the energy of the PL used to detect the ODMR signals, for which the data of Fig. 1 give $dg_\parallel/dE=0.040$ eV$^{-1}$. From Eq. (9) we find

$$dg_\parallel/dU = 2\lambda/U^2 = (\delta g_0)^2/2\lambda, \tag{10}$$

where $\delta g_0$ is the shift of the $g$ value from 2.00 at the wavelength used (0.07 at 2.65 eV). With $\lambda=-15$ meV, we find that $dg_\parallel/dU$ is of order $-0.16$ eV$^{-1}$.

In order to establish the relationship between the quantities $dg_\parallel/dE$ and $dg_\parallel/dU$, we need to consider the recombination process, which is illustrated in Fig. 5. The recombination energy is given by $E=E_0-E_D-E_A$, where $E_D$ and $E_A$ are the donor and acceptor depths and $E_0$ is a constant depending on the band gap and the average number of phonons emitted during the recombination process (we assume that the donor and acceptor are sufficiently far apart for the Coulomb interaction between them to be negligible). We assume that in an ideal GaN crystal, the $p_x$ and $p_y$ states would lie at some level $V_0$ above the valence band and would then be split by the crystal field $\Delta_{cfx}$ associated with the reduction of the site

symmetry from $C_{3v}$. Further perturbation (e.g., by nearby defects) would increase $V_0$ by an amount $V$ while at the same time changing the value of $U$. The acceptor depth is given by $E_A = V_0 + V + U/2 = V_0 + (\alpha + 1/2)U$, where we write $V = \alpha U$ and we thus find that

$$dg_{\|}/dE = -2(2\alpha + 1)^{-1} dg_{\|}/dU \tag{11}$$

where $dg_{\|}/dU$ is given by Eq. (10).

Equations (10) and (11) lead to a value for $\alpha$ of about 3.5. The *changes* in $U$ are attributed to the perturbations due to nearby defects or to strains and the value of $\alpha$ suggests that the nature of the perturbations is such that its primary effect is to increase the $z$ component of the crystal field, with a second contribution directed away from the $c$ axis. The exact value of $\alpha$ (and therefore of $dg_{\|}/dE$) will depend on the nature of the perturbation and is therefore likely to differ for crystals grown under differing conditions or with differing levels of doping. This is consistent with the the wide range of reported values for $g_{\|}$.[5,11].

As seen in Fig. 4, as $U$ gets smaller, the perpendicular $g$ value also eventually becomes smaller than 2.00. For appropriate values of $U$ it is thus possible to obtain opposite shifts in $g_{\|}$ and $g_{\perp}$. This corresponds to previous observations.[3,11].

The behavior shown in Fig. 5 is thus summarized as follows. As the acceptor is increasingly perturbed, the acceptor level moves further into the gap and the energy splitting $U$ increases. In consequence, as the PL is redshifted, $g_{\|}$ decreases and tends more closely to the spin-only value. Conversely, as the perturbation becomes weaker, so that the value of $U$ becomes smaller, $g_{\|}$ increases (accompanied eventually by a decrease in $g_{\perp}$), and it is this behavior that we next examine.

### A. The case of a pure wurtzite field

If there were no low symmetry field ($\Delta_{cfx} = 0$) and if $|\Delta_{cfz}| \gg |\lambda|$, the energy levels would be as in Fig. 2(b). The ground state Kramers doublet would, in the $|m_l, m_s\rangle$ notation, be $|1, 1/2\rangle$ and $|-1, -1/2\rangle$, which would have a finite value for $g_{\|}$ (4 in the atomic approximation) and a vanishing value of $g_{\perp}$. This can be compared with the observation by Glaser *et al.*[7] of a highly anisotropic ODMR signal with $g_{\|} = 2.193$ and $g_{\perp} = 0$ and ascribed to a *shallow* acceptor state. If the acceptor state becomes shallow, one would indeed expect high anisotropy [as with CdS (Ref. 21) and SiC (Refs. 22 and 23)], though the single atom calculation used to obtain Eqs. (7)–(9) would cease to be valid since the wave function would become delocalized. Different authors[8,19,20] have attempted to take this into account by using a value of $g_l$ of less than unity, as discussed further below.

In our discussion of the $g$ values of the deep acceptors, we have used a value for $\lambda$ of about −15 meV. In a recent paper[8] on unstrained (homo-epitaxial) GaN in which the behavior of excitons bound to shallow acceptors was studied by PL experiments in high magnetic fields (up to 25 T), it was proposed that, for the neutral acceptor states, $|\lambda|$ was an order of magnitude smaller (0.86 meV) and, further, that the crystal field along the $c$ axis was such that $W = |\Delta_{cfz}|$ was about 10.2 meV (the exact value was not critical). The ground state doublet of the neutral acceptor was found to be $|1, 1/2\rangle$ and $|-1, -1/2\rangle$ (in the $|m_l, m_s\rangle$ notation) and the first excited doublet to be almost purely $|-1, 1/2\rangle$ and $|1, -1/2\rangle$. This ground state doublet would correspond to that discussed in the present paper for the case where the crystal field away from the $c$ axis is zero ($\Delta_{cfx} = 0$). In discussing the Zeeman effects for the acceptor states in their high field PL study, Stepniewski *et al.*[8] adopt a Zeeman Hamiltonian of the form of Eq. (2). The high fields used were such that the authors could take the spin and orbital angular momenta to be decoupled (Paschen-Back regime) and they found that $g_l = 0.041$. If this value of $g_l$ is applied to the $|1, 1/2\rangle$ and $|-1, -1/2\rangle$ ground state, one obtains a value for $g_{\|}$ of 2.08 (rather than 4.00) and $g_{\perp} = 0$. To obtain the value of $g_{\|} = 2.193$ observed in ODMR studies of shallow acceptors,[7], one needs to choose $g_l = 0.1$ (see Fig. 4 for $\Delta_{cfx} = 0$).

It is interesting to contrast our approach with that of Malyshev *et al.*,[19,20] who consider the problem from the perspective of shallow acceptor wave functions. Our analysis is similar to theirs, in that we assume that the threefold orbital degeneracy of the acceptor ground state is removed by perturbing crystal fields and that the resulting three Kramers doublets are partly mixed by the spin-orbit interaction. The difference arises through our use of well-localized wave functions as a starting point. Our approach is thus likely to be valid at large acceptor depths, while that of Malyshev *et al.*[19,20] becomes appropriate at shallow depths. In an early analysis of shallow acceptor states, Malyshev *et al.*[19,20] introduced a factor $g_F$ which, for an acceptor in its ground state, corresponds to the factor $-g_l$ used in Eq. (2). They calculate that $g_F = -0.7$, which leads to $g_{\|} = 3.4$ in purely axial symmetry; this magnitude for $g_F$ thus appears to be too large.

The different choices needed for $g_l$ to fit the experimental data for shallow acceptor states in Refs. 7 and 8 and may be due to the acceptors in the two investigations being of a different type (but in neither case magnesium, since the specimens there were respectively doped with silicon or were undoped), since it is well known that the $g$ values of valence-band-related holes are sensitive to their state of binding.[21] The departure of $g_l$ from unity presumably arises because of the delocalized nature of the effective mass hole states, though the calculation of the $g$ values for such states is known to present considerable difficulty. In a recent theoretical paper,[24] with a different set of Luttinger parameters, a value of $|g_{\|}| = 2.25$ is obtained for the hole in the $A$ exciton. This compares well with the ODMR value of 2.193 for holes at shallow acceptors obtained by Glaser *et al.*[7]

### B. The effect of reduced orbital *g* factors

If we use reduced values for $g_l$ in the Hamiltonian of Eq. (2), the $g$ values become modified as in Fig. 4. It is seen that $g_{\|}$ ($=g_z$) is reduced, but that $g_{\perp}$ ($=g_x, g_y$) remain unchanged. Thus, as the low-symmetry strain component becomes weaker, it is possible to have a significant positive shift in $g_{\|}$ while at the same time having a significant negative shift in $g_{\perp}$, as observed experimentally.[3,11]

As noted above, in their approach from a different perspective, Malyshev *et al.*[19,20] predict that the $g$ factors for

shallow acceptors in GaN of purely wurtzite symmetry should be strongly anisotropic. As in the present calculation, they also find, when the low symmetry strains are sufficiently large, that the $g$ values become nearly isotropic.

The value of $g_l$, and therefore of $g_\parallel$, is likely to be very dependent on the degree of localization of the wave function of the hole trapped at the acceptor, changing from $g_l=1$ for strongly localized states to $g_l=0.1$ for the delocalized case. The behavior of $g_\parallel$ as a function of acceptor depth is thus likely to vary within the range bounded by the curves in Fig. 4 for these two values of $g_l$. The behavior of $g_\perp$ is essentially independent of $g_l$. Thus, for deep acceptors (right-hand side of Fig. 4) there are appreciable positive shifts in $g_\parallel$ but no shift in $g_\perp$ [as predicted by Eqs. (7)–(9)]. As the acceptor depth decreases (small $\Delta_{cfx}$, left-hand side of Fig. 4), there are still significant positive shifts in $g_\parallel$ and, eventually, large shifts towards zero in $g_\perp$.

### C. The nature of the crystal field at the acceptor site

It is clear, both from the present and from previous studies, that the acceptor center is produced by the incorporation of magnesium. Our analysis of the $g$ values is consistent with the magnesium substituting at a gallium site, with the hole trapped in a well-localized $p$-like orbit on one of the surrounding nitrogen atoms. If the hole is localized on a nitrogen atom adjacent to the magnesium, we have two possibilities. The first is that the nitrogen is the one located in the direction of the $c$ axis and the second is that it is one of the three located in the bond directions away from this axis. As discussed in Sec. III, the former is likely to lead to the wrong ordering of the values of $g_\parallel$ and $g_\perp$. In the latter case, the relative position of the magnesium ion and the hole would lead to both $\Delta_{cfz}$ and $\Delta_{cfx}$ being finite, even in the absence of perturbing fields due to other dopants or defects, and would thus lead to nearly isotropic $g$ values. It is also possible that the magnesium ion would be displaced from the substitutional position towards one of the nitrogens (as in the case of ZnSe:P discussed below). The model in which the hole is localized on a nitrogen atom in a non-$c$-axis bond direction relative to the magnesium also provides an explanation for the fact that the $g$ values of the electrically active magnesium acceptors at 200 meV (Ref. 5) have $g$ values close to 2.00. These acceptors are observed in both ESR and ODMR experiments to have $g_\parallel \approx 2.10$ and $g_\perp \approx 1.97$.[5] In terms of our model, the implication of this is that the acceptor level at 200 meV is such that it satisfies the criterion $|\lambda| \ll |\Delta_{cfx}|$. In other words, even for the electrically active shallow acceptors at 200 meV there is a significant low symmetry crystal field. As noted above, such a field would be a direct consequence of localization of the hole on a nitrogen in the non-$c$-axis direction. In the ODMR experiments,[5] these "shallow" acceptors are observed when monitoring the emission in the 3.2 meV region; the reported $g_\parallel$ in the region of 2.10 is consistent with extrapolation of the straight line in Fig. 1(b).

To summarize, the closeness of the $g$ values of the 200 meV acceptor to 2.00 implies that the wave function is well localized. Our model suggests that the localization is primarily on one of the nitrogens in the non-$c$-axis bond direction relative to the magnesium and that, in consequence, the crystal field symmetry is lowered, *even in the absence of perturbing fields due to nearby defects*. Since the $g$ values are very sensitive to the value of $\Delta_{cfx}$, additional contributions to $\Delta_{cfx}$ due to the presence of such defects produce further $g$ shifts, while simultaneously increasing the depth of the acceptor. It is these additional perturbations that lead to the systematic changes of the $g$ values as the ODMR detection wavelength is altered.

As a case where the symmetry of the acceptor center is lower than that of the substitutional site occupied by the dopant, an interesting parallel is provided by the example of ZnSe doped with phosphorus. In lightly doped ZnSe, phosphorus forms an acceptor level at about 85 meV.[25–28] Spin-flip Raman scattering (SFR) experiments[29–31] show that the $g$ values are those expected of valence band holes, as observed in SFR studies of nitrogen acceptors in the same material. However, unlike the nitrogen acceptors, which show the symmetry of the (strained) epitaxial layer,[29–31], the phosphorus acceptors are found[32,33] to be subject to an additional trigonal crystal field, attributable to a displacement away from the substitutional site. In contrast, ODMR studies[34] show that, in highly doped bulk ZnSe, the phosphorus forms a very deep acceptor (600 meV), in which the wave function is strongly localized and the trigonal field much stronger. The case provides an example in which the acceptor depth is very strongly influenced by the doping conditions and is in several ways similar to that of the GaN:Mg considered here.

### D. The donor states and the recombination processes

In the discussion involving the recombination energies, we have assumed that the energies of the donor states are not greatly affected by the perturbations that shift the acceptor levels. In a study of undoped GaN, Bozdog *et al.*[15] observed a range of $g$ values extending from 1.975 to 2.027 and ascribed to deep donor states. These $g$ values were accompanied by a range of emission energies attributed to recombination emission between the different types of donor and *one* type of shallow acceptor. The situation is clearly different from that observed in the present (magnesium-doped) specimens, where the values of $g_\parallel$ for the donor signals extend only over the range 1.962 to 1.972. This small range justifies our assumption that the donor depths do not change significantly in our case and that the change in emission energy in our Mg-doped specimens is primarily due to the changes in the acceptor depth. Clearly, if the depth of the donor states that participate in the recombination processes are also changing with detection wavelength, the value of $dg_\parallel/dU$ deduced from $dg_\parallel/dE$ would be different. However, the present argument would be seriously affected only if it is this change in donor depth that was *entirely* responsible for the shifts in PL energy: the work of Ref. 15 (on undoped material) shows that the shifts in the value of $g_\parallel$ for the donors would then be much larger than those observed in the present work. Our assumption that at least the major part of the shift in PL wavelength is due to variations in the acceptor depth in Mg-doped specimens is thus justified.

Other models for the recombination mechanisms that are involved in the ODMR process include two-step processes[1]

and processes in which there are large potential fluctuations that cause the energies of the donor and acceptor states to vary;[6] these models are discussed in Ref. 5. However, as explained in the preceding sections, the present data can be accounted for within the framework of a one-step (simple donor to acceptor recombination) process and we do not need to invoke additional energy levels. Our model does involve potential fluctuations (i.e., those caused by the perturbing low symmetry fields), but, as discussed in Sec. III C, the primary effect of such fluctuations is assumed to be on the energies of the acceptor states.

## IV. CONCLUSIONS

We have proposed a model which accounts for the variation in $g$ values observed for magnesium-related acceptors in GaN. The model involves holes trapped in well-localized atomic like $p$ orbits on nitrogen atoms adjacent to the magnesium dopant, the nitrogen atom involved being one of those whose bond direction is inclined to the $c$ axis. The threefold orbital degeneracy of the hole $p$ states is partly removed by the axial crystal field associated with the wurtzite structure, the twofold orbitally degenerate $p_x$ and $p_y$ being of lowest hole energy. The remaining degeneracy is removed by lower symmetry fields (due to the inherent structure of the acceptor center), leading to near-isotropic $g$ values. Further perturbations (caused by nearby defects or by strain) produce shifts in $g_{\|}$ and $g_{\perp}$ which are very sensitive to the magnitude of the these fields. At the same time, these perturbing fields lead to a change in the acceptor depth.

The model, which provides considerable insight into the nature of the crystal fields that acceptors are subject to in GaN, gives the correct $g$ values and the correct correlation between the changes in the $g$ values and the changes in the acceptor depth for reasonable choices of the parameters. It reproduces the sensitivity of the $g$ values to changes in the perturbing crystal fields. It provides an explanation of why the $g$ values of the magnesium acceptor center are close to 2.00 and why $g_{\|} > g_{\perp}$.

In the model, it is postulated that, even in "perfect" wurtzite GaN, the local symmetry of the Mg acceptor center is lower than $C_{3v}$, with $\Delta_{cfx}$ being finite. The nature of the states involved is, however, such that this decrease in symmetry is not revealed directly in the ODMR spectra (since $g_x$ and $g_y$ are almost equal, Fig. 4).

It is interesting to speculate about the nature of the shallow acceptors observed in the Si-doped material in Ref. 7, where the $g$ values are highly anisotropic. As seen from Fig. 4, this would require $\Delta_{cfx}$ to become small in comparison with $\lambda$. This may be the result of a greater delocalization of the wave function compared with the case of magnesium (such delocalization would make the hole less sensitive to the local field). One might expect an acceptor with a more delocalized hole wave function to be shallower than the 200 meV reported for magnesium, but unfortunately no data are available to confirm this.

If $\Delta_{cfx}$ does become smaller, the value of $g_{\|}$ is predicted to continue to increase while, at the same time, $g_{\perp}$ begins to undergo a negative shift (Fig. 4). If indeed the acceptor becomes shallower and the hole wave function more delocalized as $\Delta_{cfx}$ decreases, the negative shift in $g_{\perp}$ would become comparable with, and would eventually exceed, the positive shift in $g_{\|}$. This overall behavior is in agreement with observations from previous ODMR and ESR studies of GaN:Mg.[3,11] In the limit of vanishingly small low symmetry fields, the model also predicts the correct forms of the ground and near-ground Kramers doublets that are observed by other workers in studies of shallow acceptors (whose nature probably does not involve magnesium).[7,8]

Finally, the model is shown to be entirely consistent with both shallow and deep acceptor states being formed by simple substitution of a magnesium ion at a gallium site, rather than by the creation of a more complicated defect. The nearly isotropic $g$ values are a result of the symmetry of the acceptor center being less than $C_{3v}$. In this, the magnesium acceptor state may differ from those introduced by other dopants (which have the highly anisotropic $g$ values characteristic of $C_{3v}$). The depth of the magnesium acceptor is found to be dependent on the strength of low symmetry perturbation in its vicinity. Thus, different strains, induced, for example, by different growth conditions or doping levels, lead to different $g$ values and to different acceptor depths, the latter giving the possible misleading impression that there are a large number of acceptors of different origins. The need for the low symmetry fields to be small if the acceptor states are to be shallow emphasizes the need for high quality material if effective $p$-type doping is to be achieved.

## ACKNOWLEDGMENT

We are grateful for support from the EPSRC(UK) (Project No. GR/R34066) and from Universities UK for a scholarship to SZ. We thank D.M. Hofmann and A. Malyshev for helpful discussions.

*Electronic address: j.j.davies@bath.ac.uk

[1] E. R. Glaser, T. A. Kennedy, K. Doverspike, L. B. Rowland, D. K. Gaskill, J. A. Freitas, Jr., M. Asif Khan, D. T. Olson, J. N. Kuznia, and D. K. Wickenden, Phys. Rev. B **51**, 13 326 (1995).

[2] B. K. Meyer, Semicond. Semimetals **57**, 371 (1999).

[3] E. R. Glaser, T. A. Kennedy, J. A. Freitas, Jr., B. V. Shanabrook, A. E. Wickenden, D. D. Koleske, R. L. Henry, and H. Obloh, Physica B **273–274**, 58 (1999).

[4] E. R. Glaser *et al.*, Mater. Sci. Eng., B **93**, 39 (2002).

[5] E. R. Glaser, W. E. Carlos, G. C. B. Braga, J. A. Freitas Jr., W. J. Moore, B. V. Shanabrook, R. L. Henry, A. E. Wickenden, D. D. Koleske, H. Obloh, P. Kozodoy, S. P. DenBaars, and U. K. Mishra, Phys. Rev. B **65**, 085312 (2002).

[6] M. A. Reshchikov, G.-C. Yi, and B. W. Wessels, Phys. Rev. B **59**,

13 176 (1999).
[7] E. R. Glaser, J. A. Freitas, Jr., B. V. Shanabrook, D. D. Koleske, S. K. Lee, S. S. Park, and J. Y. Han, Phys. Rev. B **68**, 195201 (2003).
[8] R. Stepniewski, A. Wysmolek, M. Potemski, K. Pakula, J. M. Baranowski, I. Grzegory, S. Porowski, G. Martinez, and P. Wyder, Phys. Rev. Lett. **91**, 226404 (2003).
[9] H. Alves, F. Leiter, D. Pfisterer, D. M. Hofmann, B. K. Meyer, S. Einfeld, H. Heinke, and D. Hommel, Phys. Status Solidi C **70**, 1770 (2003).
[10] J.-M. Spaeth and H. Overhof, *Point Defects in Semiconductors and Insulators* (Springer Verlag, Berlin 2003).
[11] D. M. Hofmann, W. Burkhardt, F. Leiter, W. von Frster, H. Alves, A. Hofstaetter, B. K. Meyer, N. G. Romanov, H. Amano, and I. Akasaki, Physica B **273–274**, 43 (1999).
[12] J. J. Davies, G. N. Aliev, S. J. Bingham, D. Wolverson, S. Stepanov, B. Yavich, and W. N. Wang, Phys. Rev. B **67**, 035203 (2003).
[13] G. N. Aliev, S. Zeng, D. Wolverson, J. J. Davies, S. J. Bingham, P. Parbrook, and T. Wang (unpublished).
[14] W. E. Carlos, J. A. Freitas, Jr., M. A. Khan, D. T. Olson, and J. N. Kuznia, Phys. Rev. B **48**, 178 78 (1993).
[15] C. Bozdog, G. D. Watkins, H. Sunakawa, N. Kuroda, and A. Usui, Phys. Rev. B **65**, 125207 (2002).
[16] J. Schneider, J. Phys. Chem. Solids **31**, 337 (1970).
[17] R. K. Watts, W. C. Holton, and M. de Wit, Phys. Rev. B **3**, 404 (1971).
[18] J. S. Griffith, *The Theory of Transition Metal Ions* (Cambridge University Press, Cambridge, 1961).
[19] A. V. Malyshev, I. A. Merkulov, and A. V. Rodina, Fiz. Tverd. Tela (S.-Peterburg) **40**, 1002 (1998) [Phys. Solid State **40**, 917 (1998). Note: typographical errors in the tables of this paper are corrected in Ref. 23].
[20] A. V. Malyshev, I. A. Merkulov, and A. V. Rodina, Phys. Status Solidi B **210**, 865 (1998).
[21] J. L. Patel, J. E. Nicholls, and J. J. Davies, J. Phys. C **14**, 139 (1981).
[22] Le Si Dang, K. M. Lee, G. D. Watkins, and W. J. Choyke, Phys. Rev. Lett. **45**, 390 (1980).
[23] P. G. Baranov, V. A. Vetrov, N. G. Romanov, and V. I. Sokolov, Fiz. Tverd. Tela (Leningrad) **27**, 3459 (1985) [Sov. Phys. Solid State **27**, 2085 (1985)].
[24] A. V. Rodina, M. Dietrich, A. Göldner, L. Eckey, A. Hoffmann, Al. L. Efros, M. Rosen, and B. K. Meyer, Phys. Rev. B **64**, 115204 (2001).
[25] T. Yao and K. Okada, Jpn. J. Appl. Phys., Part 1 **25**, 821 (1986).
[26] G. Neu, C. Morhain, E. Tournié, and J.-P. Faurie, J. Cryst. Growth **184/185**, 515 (1998).
[27] L. C. Calhoun and R. M. Park, J. Appl. Phys. **85**, 490 (1999).
[28] G. Neu, E. Tournié, C. Morhain, M. Teisseire, and J.-P. Faurie, Phys. Rev. B **61**, 15 789 (2000).
[29] C. Orange, B. Schlichtherle, D. Wolverson, J. J. Davies, T. Ruf, K. I. Ogata, and S. Fujita, Phys. Rev. B **55**, 1607 (1997).
[30] W. Heimbrodt, C. L. Orange, D. Wolverson, J. J. Davies, K. Kimura, and T. Yao, Phys. Rev. B **56**, 6889 (1997).
[31] C. L. Orange, W. Heimbrodt, D. Wolverson, and J. J. Davies, J. Cryst. Growth **184/185**, 510 (1998).
[32] J. J. Davies, D. Wolverson, S. Strauf, P. Michler, J. Gutowski, M. Klude, K. Ohkawa, D. Hommel, E. Tournié, and J.-P. Faurie, Phys. Rev. B **64**, 205206 (2001).
[33] D. Wolverson, J. J. Davies, S. Strauf, P. Michler, J. Gutowski, M. Klude, D. Hommel, K. Ohkawa, E. Tournié, and J.-P. Faurie, Phys. Status Solidi B **229**, 257 (2002).
[34] J. E. Nicholls and J. J. Davies, J. Phys. C **12**, 1917 (1979).