Magnetic resonance and the structure of magnesium acceptors in gallium nitride

J. J. Davies*
Department of Physics, University of Bath, Bath BA2 7AY, United Kingdom
(Received 22 April 2013; revised manuscript received 7 June 2013; published 24 June 2013)

In recent years there have been several theoretical and experimental investigations concerned with the detailed structure of the acceptor states in Mg-doped GaN. Thus, the shallow effective-mass-like acceptor has been attributed to simple substitutional Mg at Ga sites in unstrained regions of the material, while earlier suggestions that the Mg is associated with H appear to have been discounted by more recent studies. Deeper acceptor states have also been attributed to simple substitutional Mg, but in strained regions. The present paper makes use of the extensive data available from electron spin resonance and optically detected magnetic resonance to confirm these assignments and to highlight further the crucial role played by strain in influencing the detailed nature of the acceptor states. In particular, the neutral deep acceptor states are found to be formed by localization of the holes in p-like orbits on N atoms that lie in the basal plane, rather than along the c axis, relative to the Mg dopant.

DOI: 10.1103/PhysRevB.87.235208 PACS number(s): 76.70.Hb, 61.72.uj, 71.55.Eq, 78.55.Cr

I. INTRODUCTION

Despite the outstanding technological developments of light-emitting devices based on GaN, there remains a lack of consensus on the detailed structure of the acceptor states involved in p-type doping of the material. The only effective p-type dopant appears to be Mg and recent studies[1] have led to the conclusion that there are then at least two types of acceptor states, designated $A1$ and $A2$. In Ref. 1 it was concluded that, at low temperature, acceptor $A1$ is associated with an acceptor-bound exciton (ABE) recombination at 3.466 eV and a donor-acceptor pair (DAP) recombination at 3.27 eV, while $A2$ leads to ABE and DAP emission at 3.454 and 3.15 eV, respectively.[1] The atomic structure of these acceptor states has been the object of recent experimental and theoretical investigations.[1–4] Thus, in Ref. 1 it was proposed that the $A1$ (the so-called shallow) acceptor is formed by the association between Mg and H atoms and that $A2$ (the so-called deep acceptor) is due to unassociated substitutional Mg. This attribution appeared to be supported by the calculations of the authors of Ref. 3, where the shallow acceptor was calculated to have a delocalized wave function and the deep acceptor to have a wave function localized on a ligand N that lies on the c axis relative to the Mg (the axial arrangement). This contrasted with an earlier calculation,[2] which predicted that in the deep acceptor the hole is instead localized on a N that lies in the basal plane relative to the Mg (the basal or planar arrangement). Very recently,[4] evidence has been presented (i) that the $A1$ acceptor is not in fact formed by association between H and Mg and that it is instead simply formed from substitutional Mg alone, while (ii) the $A2$ acceptor is also formed from substitutional Mg, in this case perturbed by its proximity to a basal stacking fault. Evidence for a third Mg-related acceptor has also recently been reported.[5]

Historically, one of the most successful techniques for elucidating the microscopic structure of dopant centers in semiconductors is magnetic resonance [optically detected magnetic resonance (ODMR) and electron spin resonance (ESR)] and several such studies have been carried out on epitaxial GaN (Refs. 6–13). The purpose of the present paper is to show that one can distinguish between the various models for the different acceptor states by making use of the extensive data from these experiments. It will be shown that the ESR and ODMR spectra are consistent with a simple model in which both the $A1$ and $A2$ acceptors are indeed formed from substitutional unassociated Mg (as concluded in Ref. 4). Further, the data lead to a model for the $A2$ neutral acceptor in which the hole is localized in a N orbit in the basal arrangement (as predicted by the authors of Ref. 2 but in conflict with the conclusion of the authors of Ref. 3). The role of strain is confirmed to be crucial in determining the parameters that describe the magnetic resonance spectra.

II. MAGNETIC RESONANCE BACKGROUND

Both electron spin resonance (ESR) and optically detected magnetic resonance (ODMR) have been used to obtain spectra attributable to both donor and acceptor states in GaN (Refs. 6–13). In the case of acceptors, signals can be divided into two categories.

(i) Acceptors with highly anisotropic g tensors, whose symmetry reflects that of the wurtzite crystal structure and which are attributable to "shallow" effective-mass-like (EM) centers.[12,13] In ODMR in Mg-doped GaN with low strain, these acceptors are observed by monitoring the 3.27 eV photoluminescence (PL), so that they can be identified as the $A1$ acceptors. The acceptors have effective spins of $1/2$, with g values of $g_{\parallel} = 2.19 \pm 0.01$ and $g_{\perp} \sim 0$, for magnetic field directions along and perpendicular to the c axis.[13]

(ii) Acceptors with g tensors of much smaller but measurable anisotropy, again with an apparent symmetry appropriate to the crystal structure. These spectra are attributed to "deep" acceptors.[6–11] The ESR spectra from these acceptors are also characterized by effective spins of $1/2$, but with g values $g_{\parallel} = 2.097 \pm 0.004$ and $g_{\perp} = 1.994 \pm 0.004$ (Ref. 10). Similar g values are obtained from ODMR experiments[6–11] but depend on the wavelength of the recombination emission monitored in the experiment. The line widths of the signals are large, typically 10 mT or more. The ODMR signals can be detected over a wide range of PL energies and we shall show that they are consistent with the acceptors in the neutral state being formed from Mg substituting at Ga sites with holes localized on nitrogen atoms in the basal planar, rather than the axial

 ©2013 American Physical Society

configuration. The basal arrangement occurs in the presence of nonaxial local strain which lowers the local symmetry at the Mg site. As discussed later, the $A2$ acceptors are a particular case of such localized centers.

We shall show that, paradoxically, the $A1$ acceptor, which has high local symmetry, leads to magnetic resonance spectra which *appear* to have much greater anisotropy than those found for the $A2$ acceptors, which have lower local symmetry.

A. Acceptor g values

1. Crystal fields of purely axial symmetry

It is convenient to begin with the "deep" acceptors. We consider first the possibility that the hole on the neutral acceptor is in a localized orbit on a N atom along the c axis relative to the Mg dopant (the axial case: this is the stable configuration predicted by the calculation of the authors of Ref. 3). The hole is subjected to a crystal field which can be represented by the orbital angular momentum operator $\Delta[l_z^2 - l(l+1)/3]$, where the z direction is along the c axis. In this case, there are two contributions to Δ: one a consequence of the wurtzite structure and the other due to the presence of the Mg dopant. The appropriate Hamiltonian can be written as

$$H = \Delta\left[l_z^2 - l(l+1)/3\right] + \lambda \mathbf{l}\cdot\mathbf{s} + \mu_B(g_l\mathbf{l} + g_s\mathbf{s})\cdot\mathbf{B}, \qquad (1)$$

where the second and third terms represent, respectively, the spin-orbit coupling and the interaction with an applied magnetic field $\mathbf{B}$. The factors g_s and g_l are taken to be 2.0023 and 1, as for electrons in atomic orbits.[14]

To a first approximation, we take the hole to be localized in an orbit formed from N $2p$ states. For the hole to be in an orbit aligned along the c axis, Δ must be positive, so that the $2p_z$ orbital singlet lies lowest in energy. Equation (1) leads to g values for the field along and perpendicular to the c axis given by (see, e.g., Ref. 11)

$$g_\parallel \approx 2.00, \quad g_\perp \approx 2.00 - 2\lambda/\Delta,$$

where the spin-orbit coupling parameter λ (which is assumed small in comparison with Δ) is negative for holes. The value of $g_\perp$ is therefore predicted to be greater than $g_\parallel$, clearly in disagreement with experiment. The model for the deep acceptor in which the hole in the neutral state is localized in the axial configuration (i.e., with Δ of positive sign) must therefore be discarded.

If on the other hand Δ is negative, an orbital doublet lies lowest, which is then split by spin-orbit coupling, so that the energetically lowest state is of the form $(|1,1/2\rangle + |-1,-1/2\rangle)/\sqrt{2}$ and has $g_\perp \approx 0$, with $g_\parallel$ in the range 2 to 4. Again, clearly, these values do not fit the data for the deep acceptor. However, they do agree with the data for the shallow ("effective mass") acceptors ($g_\parallel = 2.19 \pm 0.01$ and $g_\perp \sim 0$) (Refs. 12,13). The reduction of $g_\parallel$ from the value of 4.0 predicted for a highly localized orbit of the type considered above can be accounted for by taking the orbital g value g_l to be less than unity.[15,16] Similar g values for shallow acceptors have been observed in SiC (Ref. 17) and CdS (Ref. 18) and possible reasons for such a reduction in $g_\parallel$ are discussed in Ref. 17. Thus, the $A1$ acceptor can be identified as a Mg ion substituting at a Ga site under the influence of a crystal field (with delta negative) which is either (i) purely axial (as would be the case if the Mg were in strain-free regions) or (ii) such that the effects of nonaxial fields (discussed below) are small. The latter would be the case, for example, for acceptors of the type considered in Refs. 1,3, where the Mg is associated with a H atom, with the acceptor wave function being delocalized: however, in view of the conclusions of the authors of Ref. 4 this model must now be discounted.

In contrast, the g values commonly observed for the "deep" acceptors are not consistent with substitutional Mg with a purely axial crystal field of either sign. To reproduce these g values, it is necessary to introduce strains of lower symmetry, as considered in the following subsection.

2. Crystal fields of symmetry lower than axial

If Δ is negative for the deep acceptors (as for the shallow acceptors), then the application of an additional crystal field of symmetry lower than axial will act to remove the degeneracy of the low-lying orbital doublet, even in the absence of any spin-orbit coupling. For a deep acceptor in which the hole is localized on a N atom other than one on the c axis relative to the Mg, such an additional field is provided by the presence of the Mg atom itself (this is the basal arrangement discussed in Refs. 2 and 3). We can then approximate the crystal fields due to the wurtzite structure and due to the perturbing Mg as $\Delta[l_z^2 - l(l+1)/3]$ and $\delta[l_\zeta^2 - l(l+1)/3]$, respectively, where the ζ axis is at an angle α to the c axis, where $\alpha \approx 105^\circ$ (as discussed later in Sec. II B, there must in addition be further contributions to the spin Hamiltonian caused by the effects of low-symmetry strains). The orbital degeneracy is removed by the term in δ and further mixing of the states is caused by the spin-orbit coupling.

The resulting g tensor has principal axes which are no longer along and perpendicular to the crystal c axis. There are six possible orientations for the axis that links the Mg and the localized hole and the corresponding g values for different directions of the magnetic field are shown in Fig. 1 (obtained by a numerical solution for the eigenvalues of the spin Hamiltonian containing Δ and δ) for two planes in which the magnetic field direction can be altered. The value of $\delta = 22.5|\lambda|$ is chosen so as to reproduce the experimental g value when the magnetic field is along the c axis (if the sign of δ were reversed, the sets of data in the two panels of Fig. 1 would be interchanged). The value of Δ determines the spread in g values when the field is at 90° to the c axis and its exact value is not critical provided that $\Delta \gg \delta$. The value of λ (of order several meV) is implicitly assumed large in comparison to the Zeeman energies.

The line widths of the signals observed in the ESR spectra[10] are of order of 12 mT, which at 9 GHz corresponds to a range of 0.08 in the g value. The line widths in ODMR experiments are also large, for example 20 mT at 23 GHz, corresponding to a range of g values of 0.05. The differences between the curves shown in Fig. 1 for the different orientations of the acceptor axes would therefore not be experimentally resolvable, so that an overall angular dependence of the signals would be described by a weighted average, as shown by the dashed line. The observed spectra therefore *appear* to have an axial symmetry relative to the c axis, even though the actual g tensors have lower symmetry. The weighted average has a

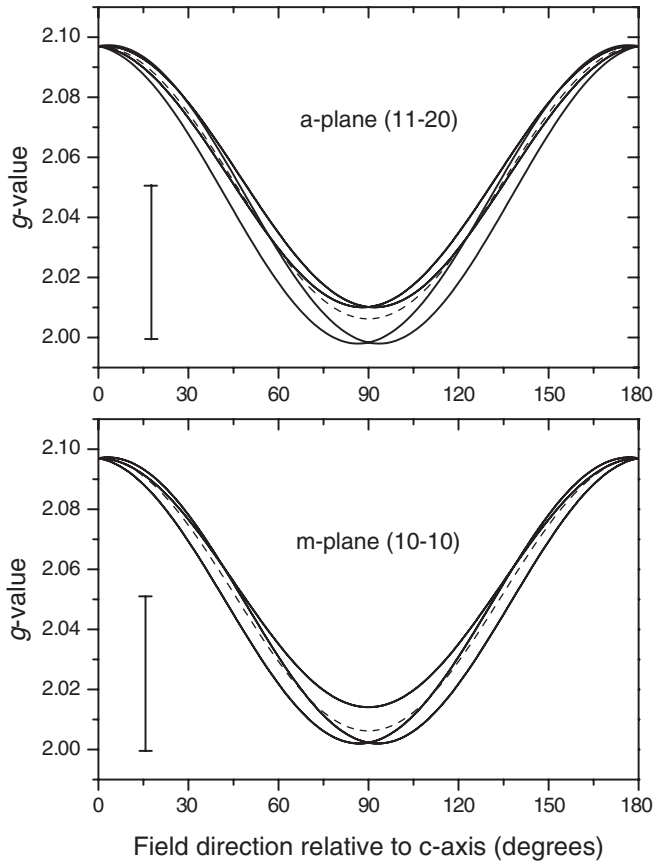

FIG. 1. The calculated g values for the differently orientated Mg basal-type deep acceptor centers as a function of the direction of the magnetic field relative to the c axis, for two different planes containing the field. The broken line is the weighted average of the g values for a given field direction. The error bar indicates the minimum line width observed in the magnetic resonance experiments (see text) expressed as a variation in g value. This line width is such that the detailed anisotropy is not resolved, so that the angular variation appears to have axial symmetry, as represented by the broken line. For both graphs, $\Delta = -100|\lambda|$, $\delta = 22.5|\lambda|$, and $\lambda = -15$ meV.

g value of the form $\sqrt{(g_\parallel^2 \cos^2\theta + g_\perp^2 \sin^2\theta)}$, where θ is the angle between the magnetic field and the crystal c axis.

The calculated values of $g_\parallel$ and $g_\perp$ over a wide range of δ/λ are shown in Fig. 2. If $|\Delta| \gg |\delta| \gg |\lambda|$, then, following a calculation similar to that in Ref. 11, these average g values can be expressed as

$$g_\parallel \approx 2.00 - 2\lambda/|\delta \sin^2(\alpha)|, \quad g_\perp \approx 2.00. \tag{2}$$

The calculation assumes that the hole is located in a N $2p$ orbit, whereas in reality the wave function is also likely to have some s character. However, this will not alter the anisotropy $g_\parallel > g_\perp$ predicted by Eq. (2). We therefore have $g_\parallel > g_\perp$, in much better agreement with the experimental data for deep acceptors.[6–11]

B. Correlation between g values and strain

The calculation made above of the g values for the deep acceptors assumes two crystal fields at the N site: (i) one (Δ) of axial symmetry, appropriate to the wurtzite crystal structure

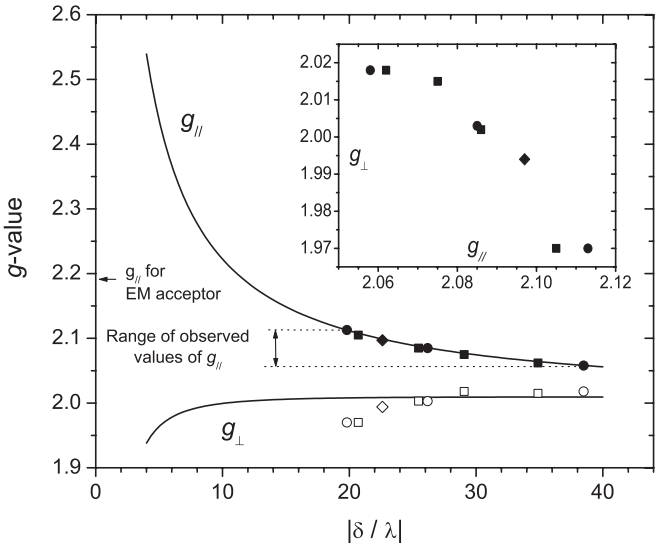

FIG. 2. Calculated values of $g_\parallel$ and $g_\perp$(averaged as in Fig. 1) as a function of $|\delta/\lambda|$. The values of $g_\parallel$ and $g_\perp$ observed experimentally are correlated, as shown in the inset [squares (Ref. 10) and circles (Ref. 8) in the inset are from ODMR and the diamond is from ESR (Ref. 10)]. The values for $g_\parallel$ (filled symbols) have been plotted so as to lie on the upper curve in the main diagram and the values of $g_\perp$ (open symbols) are added at the same values of $|\delta/\lambda|$ as for the corresponding values of $g_\parallel$.

and (ii) the other (δ) due to the presence of the Mg atom which lies approximately along a bond direction (in the basal arrangement). In reality, the situation is more complicated, as demonstrated by the fact that the acceptor g values are not unique, but cover a range[8,10] extending from $g_\parallel = 2.066$ and $g_\perp = 2.02$ to $g_\parallel = 2.11$ and $g_\perp = 1.97$, with $g_\parallel$ correlated with $g_\perp \sim 0$ (see the inset to Fig. 2). In the ODMR experiment, different sets of g values are obtained for different samples. Furthermore, if the energy of the PL that is being monitored is altered, the values of $g_\parallel$ change in a continuous manner, with $g_\parallel$ decreasing as the detection energy of the PL gets smaller (see, e.g., Fig. 6 of Ref. 10). The overall behavior is attributable to the presence of additional, varying strains at the acceptor site: these strains lead to additional contributions to Δ and δ and also to variations in the acceptor depth.

The possible role of strain variations was discussed qualitatively in Refs. 9,13 and also in Ref. 12, where it was suggested that the effective mass acceptors were in strain-free regions and that the other acceptors were in regions where there was a range of strains. This is supported by the recent evidence found in Ref. 4, where the neutral $A1$ acceptor is proposed to be substitutional Mg in strain-free regions (with the hole delocalized) and the $A2$ acceptor also to be substitutional Mg, but in association with basal stacking faults (with the hole localized). Recent structural studies[19] provided evidence that there is a preferential distance between the Mg dopant and the stacking fault, and this provides a natural explanation for the depth of the $A2$ acceptor being well defined.

If values of δ/λ are chosen so that the experimental values of $g_\parallel$ lie on the upper branch of the curves in Fig. 2, the values of $g_\perp$ at the higher range of δ/λ are found to lie close to the lower branch. As δ/λ is decreased, the values of $g_\parallel$ and $g_\perp$ can

TABLE I. Apparent g values for GaN acceptor states, as discussed in the text.

Crystal field	$g_\parallel$	$g_\perp$	Comments	Experiment
Δ negative with $\delta \approx 0$	$4 > g_\parallel > 2$	$g_\perp \approx 0$	Prediction for shallow acceptors	Refs. 12,13.
Δ negative with δ finite and $\lvert\delta\rvert < \lvert\Delta\rvert$	$g_\parallel > 2$	$g_\perp \approx 2$ ($g_\perp < 2$ if δ small)	Prediction for basal deep acceptors	Refs. 6–11.
Δ positive	$g_\parallel \approx 2$	$g_\perp > 2$	Prediction for axial deep acceptors	Not observed

no longer be fitted simultaneously at the same value of δ/λ. If δ/λ is chosen so as to fit $g_\parallel$ (as shown), then $g_\perp$ starts to fall beneath the predicted curve as δ/λ becomes smaller. This suggests that the simple model in which the hole is localized on a single N atom (and on which Fig. 2 is based) is starting to break down as δ/λ becomes smaller and that delocalization is becoming important. As noted earlier, as δ becomes smaller, $g_\perp$ is expected to fall towards zero.

III. CONCLUSION

A fully consistent description of the behavior of acceptor states thus emerges and can be summarized as follows (see Table I).

All the data for the $A1$ acceptor are consistent with it being formed by substitutional, isolated Mg in strain-free regions of the material. The crystal field parameter Δ is negative.

The deep acceptors are also formed by substitutional Mg, but in regions of the specimen which are strained and which, for the neutral acceptor state, stabilize a situation in which the hole is localized in a p-like orbit on a N atom in the basal arrangement (again, Δ is negative and there are finite nonaxial crystal field contributions). This conclusion differs from that of the authors of Ref. 3 but agrees with that of the authors of Ref. 2. A conclusion similar to the present one is obtained from optical studies in Ref. 5.

As the nonaxial strain is increased, the apparent g values of the deep acceptors are predicted to converge to 2.00 (see Fig. 1). Experimentally, as this occurs, the energy of the PL required for their detection in ODMR decreases. Furthermore, a continuous range of acceptor g values is observed, correlated with the detection energy. This suggests that there is a continuous range of acceptors whose depth is dependent on local strain, possibly caused by association with other defects.

In the particular case of the $A2$ acceptor, the strain is well defined, possibly because of the association of the Mg with a stacking fault at a preferential distance,[4,19] so that the acceptor depth is also well defined. A particularly interesting feature is that ODMR signals with g values $g_\parallel = 2.11$ and $g_\perp = 1.97$ characteristic of localized acceptor wave functions can be detected from Mg-doped metal-organic chemical vapor deposition (MOCVD) heteroepitaxial layers[8,10,13] by monitoring PL with energy in the region of 3.27 eV. In contrast, when the emission of this energy is monitored from Mg-doped homoepitaxial specimens, the observed g values ($g_\parallel = 2.19$ and $g_\perp \sim 0$) are characteristic of the effective-mass-like $A1$ acceptors, confirming that under certain circumstances acceptors with localized wave functions can have similar depths to those of acceptors whose wave functions are delocalized.

If the acceptor were to become sufficiently deep. this would lead to the so-called blue emission in the range around 2.9 eV, which ODMR experiments strongly suggest to be due to donor-acceptor recombination. This emission, commonly observed from material grown by MOVCD, would then be the consequence of large local nonaxial strains, possibly associated with the incorporation of H. If such strains were small or absent, the blue emission would not necessarily be observed.

An important consequence of the analysis is that a full understanding and control of the strain distributions in the material continues to be vital to improved device performance.

ACKNOWLEDGMENTS

Daniel Wolverson and Kevin P. O'Donnell are thanked for their helpful comments and the authors of Ref. 4 for making available a preprint of their work.

*j.j.davies@bath.ac.uk

[1] B. Monemar, P. P. Paskov, G. Pozina, C. Hemmingsson, J. P. Bergman, T. Kawashima, H. Amano, I. Akasaki, T. Paskova, S. Figge, D. Hommel, and A. Usui, Phys. Rev. Lett. **102**, 235501 (2009).

[2] S. Lany and A. Zunger, Appl. Phys. Lett. **96**, 142114 (2010).

[3] J. L. Lyons, A. Janotti, and C. G. Van de Walle, Phys. Rev. Lett. **108**, 156403 (2012).

[4] B. Monemar, S. Khromov, G. Pozina, P. Paskov, P. Bergman, C. Hemmingsson, L. Hultman, H. Amano, Xing Li, and H. Morkoç, Jpn. J. Appl. Phys. **52**, 08JJ03 (2013).

[5] G. Callsen, M. R. Wagner, T. Kure, J. S. Reparaz, M. Bugler, J. Brunnmeier, C. Nenstiel, A. Hoffmann, M. Hoffmann, J. Tweedie, Z. Bryan, S. Aygun, R. Kirste, R. Collazo, and Z. Sitar, Phys. Rev. B **86**, 075207 (2012).

[6] 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**, 13326 (1995).

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

[8] 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**, 58 (1999).

[9]D. M. Hofmann, W. Burkhardt, F. Leiter, W. von Förster, H. Alves, A. Hofstaetter, B. K. Meyer, N. G. Romanov, H. Amano, and I. Akasaki, Physica B **273**, 43 (1999).

[10]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).

[11]G. N. Aliev, S. Zeng, J. J. Davies, D. Wolverson, S. J. Bingham, P. J. Parbrook, and T. Wang, Phys. Rev. B **71**, 195204 (2005).

[12]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).

[13]E. R. Glaser, M. Murthy, J. A. Freitas, Jr., D. F. Storm, L. Zhou, and D. J. Smith, Physica B **401**, 327 (2007).

[14]When considering delocalized electrons, Malyshev *et al.*[15,16] allowed g_l to be less than unity.

[15]A. V. Malyshev, I. A. Merkulov, and A. V. Rodina, Fiz. Tverd. Tela (St. Petersburg) **40**, 1002 (1998) [Phys. Solid State **40**, 917 (1998)].

[16]A. V. Malyshev, I. A. Merkulov, and A. V. Rodina, Phys. Status Solidi B **210**, 865 (1998).

[17]Le Si Dang, K. M. Lee, G. D. Watkins, and W. J. Choyke, Phys. Rev. Lett. **45**, 390 (1980).

[18]J. L. Patel, J. E. Nicholls, and J. J. Davies, J. Phys. C **14**, 139 (1981).

[19]S. Khromov, C. G. Hemmingsson, H. Amano, B. Monemar, L. Hultman, and G. Pozina, Phys. Rev. B **84**, 075324 (2011).