Magneto-optical studies of the 0.88-eV photoluminescence emission in electron-irradiated GaN

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Properties of the 0.88-eV photoluminescence (PL) in electron-irradiated wurtzite GaN have been investigated in detail by a combination of various magneto-optical techniques, including Zeeman measurements of PL, optically detected magnetic resonance (ODMR), and level anticrossing (LAC). ODMR observed by monitoring the PL emission is demonstrated to originate from a spin triplet. The symmetry of the corresponding defect is shown to be rhombic with its principal axes pointing into the high-symmetry directions $Z=[0001]$, $Y=[1\bar{1}00]$, and $X=[11\bar{2}0]$. From the Zeeman measurements the emission is shown to arise from an optical transition between a singlet excited state and the singlet ground state, providing convincing evidence for indirect detection of the spin triplet ODMR. LAC investigations of the same PL emission reveal two LAC lines, among which one is related to the spin triplet detected in ODMR.

I. INTRODUCTION

Group III nitrides have been a subject of intense scientific research and rapid technological developments in recent years because of their great potential in applications for a variety of high-performance opto-electronic and electronic devices.[1] One of the most outstanding achievements undoubtedly is the realization of efficient and long-lifetime light-emitting devices operating in the much-needed blue and UV spectral range. With regard to many fundamental issues such as defects, in particular intrinsic point defects, however, our knowledge has so far remained very limited. Only very few defects, mostly transition metals like iron, have been identified unambiguously by, e.g., magnetic resonance techniques.[2] A better understanding of defect properties and their role in device performance is essential for improving and optimizing material and device parameters.

Electron irradiation of semiconductors is not only of technological importance in device fabrication. It is also a powerful tool for investigations on intrinsic defects and/or their complexes with common impurities. This is due to the fact that electron irradiation creates only primary intrinsic defects such as vacancies, self-interstitials, antisites, and their complexes with impurities already present in a crystal. No additional impurities are introduced so that the process of defect formation and interaction is relatively simple. Though electron irradiation has widely been employed in other semiconductors and has contributed a great deal to our present understanding of intrinsic defects in those materials,[3] its application in GaN has just started to emerge.[4–12]

Recent studies have shown that one of the dominant photoluminescence (PL) emissions, which appear after electron irradiation of wurtzite GaN is the so-called 0.88-eV PL emission.[4,7,8] This emission consists of a no-phonon (NP) line near 0.88 eV, a hot no-phonon line NP* appearing at elevated temperature, and a richly structured phonon sideband. By monitoring the 0.88-eV PL emission, an ODMR (optically detected magnetic resonance) signal typical for a spin-triplet defect (denoted as $L2$) was observed.[4,11,12] It has not been unambiguously shown, however, if this spin triplet is the exact excited state involved in the electronic transition leading to the 0.88-eV PL emission.

In this work we shall present experimental evidence from a combination of various magneto-optical spectroscopy techniques, suggesting that the spin triplet is in fact not the same defect level giving rise to the 0.88-eV PL emission. It is instead shown from the Zeeman measurements to originate from an optical transition between a singlet excited state to the singlet ground state. A detailed analysis of the PL, Zeeman, level anticrossing (LAC), and ODMR results provides useful information on the electronic structure of the defect levels and the recombination process involved in the 0.88-eV PL emission. A close examination of the crystallographic directions of the samples by x-ray-diffraction (XRD) pole figures has made possible a one-to-one correlation of these directions with the symmetry axes of the spin-triplet defect.

II. EXPERIMENTAL DETAILS

The experimental setup used for the Zeeman studies was based on an Oxford superconducting magnet producing magnetic fields up to 14 T, in which the temperature could be varied between 1.5 K and room temperature. The resulting luminescence was spectrally dispersed by a 0.85-m double-grating monochromator. The ODMR and LAC experiments were performed in a modified Bruker EPR spectrometer working at X band (~9.23 GHz) equipped with a helium flow cryostat. Temperatures as low as 2.5 K could be achieved. For spectral dependence studies a 0.25-m grating monochromator was inserted into the light beam on the de-

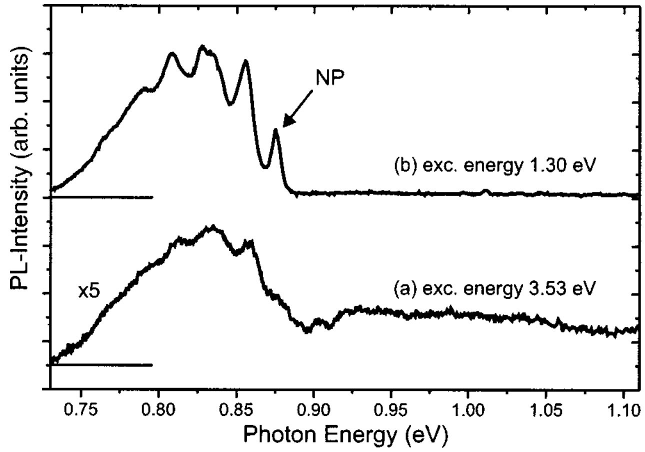

FIG. 1. Photoluminescence (PL) spectra of an electron-irradiated GaN sample under above band-gap excitation with the UV line of an Ar^+ laser (a) and selective excitation using a Ti: sapphire laser (b). In this sample the 0.88-eV emission is strongly enhanced by the selective excitation. The base line is indicated by the horizontal lines.

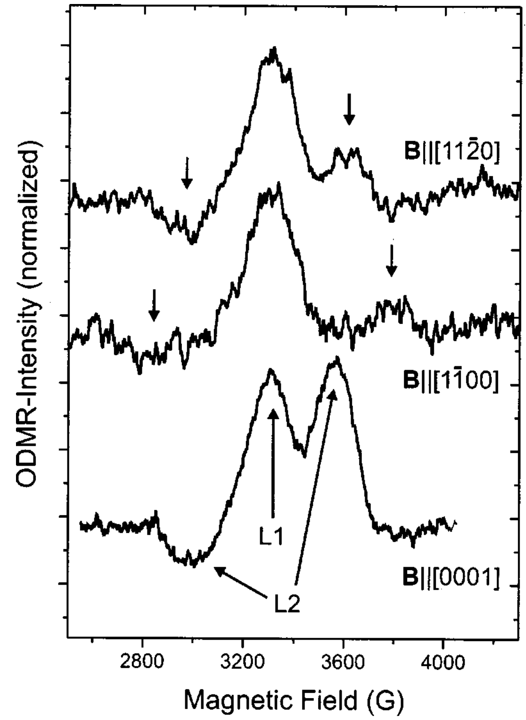

FIG. 2. Optically detected magnetic resonance (ODMR) spectra at 2.5 K with the magnetic field oriented along the high-symmetry directions of the wurtzite crystal. The biggest splitting of the triplet lines occurs when **B** is along $[1\bar{1}00]$. The microwave frequency used was 9.2275 GHz.

tection side. In high-resolution PL experiments, a 0.85-m double-grating monochromator was used. The luminescence was excited with the 351-nm UV line of an Ar^+ laser for the above band-gap excitation, and with the 1090-nm line of the Ar^+ laser or a tunable (700–1000 nm) Ti: sapphire laser for selective excitation of the 0.88-eV PL emission. For luminescence detection, a liquid-nitrogen-cooled Ge detector (model North Coast) was used.

The experiments were performed on a variety of wurtzite GaN layers grown by metal-organic chemical-vapor deposition (MOCVD) or hydride vapor phase epitaxy (HVPE) on sapphire or a 6H-SiC substrate. The thickness of the layers varies from a few micrometers up to 200 μm. Before electron irradiation the conductivity of the samples ranged from *n*-type over compensated to *p*-type (obtained by Zn or Mg doping). They were irradiated with 2.5-MeV electrons at room temperature with a dose from $1\times10^{17}\,cm^{-2}$ up to $4\times10^{18}\,cm^{-2}$.

The crystallographic axes were determined using XRD pole figures. The texture analysis was carried out in a Philips X'pert MRD system equipped with a four-circle goniometer using a pinhole primary collimator and a parallel-plate secondary collimator.

III. RESULTS

After electron irradiation of wurtzite GaN, two new PL bands dominate in the near-infrared region. One of them, which is broad and unstructured, has its maximum intensity at around 0.93 eV. The other one has a rather narrow NP line around 0.88 eV and is followed by a rich and structured phonon-assisted sideband. Even though both emissions are commonly observed in all irradiated samples their relative intensities depend on the initial conductivity (type and carrier concentration) before irradiation,[8] and also on a number of experimental parameters such as irradiation dose, measuring temperature, and photoexcitation condition. These properties of the PL emissions have been given earlier.[8–10] In the present work we will focus on magneto-optical properties of the 0.88-eV PL emission. For an easy reference a typical PL spectrum from the samples with the UV (i.e., above band gap) excitation is shown in Fig. 1(a).

A. ODMR experiments

ODMR spectra monitoring the 0.88-eV PL emission obtained with above band-gap excitation and when the external magnetic field is along the main crystallographic axes, i.e., **B**$\|[0001]$, **B**$\|[1\bar{1}00]$, and **B**$\|[11\bar{2}0]$ are shown in Fig. 2. The spectra consist of the nearly isotropic $L1$ and two lines of the spin-triplet center $L2$. $L1$ was shown earlier to originate from the 0.93-eV PL (Refs. 11 and 12) outside the scope of the present paper, and will therefore not be discussed any further below. The largest splitting between the two $L2$ lines occurs in the (0001) plane when **B**$\|[1\bar{1}00]$.

In Ref. 12 the spin-Hamiltonian parameters for $L2$ were determined to be $g_x=2.002$, $g_y=1.995$, $g_z=2.002$, $D_x=\pm0.33\,\mathrm{GHz}$, $D_y=\mp0.87\,\mathrm{GHz}$, and $D_z=\pm0.54\,\mathrm{GHz}$. *X*, *Y*, and *Z* denote the principal axes of the defect determining its symmetry. One of these axes, denoted as *Z*, was shown to be along the *c* axis of the hexagonal crystal. The other two axes were claimed to lie along $[1\bar{1}00]$ and $[11\bar{2}0]$, respectively. This earlier study was, however, not able to determine whether *X* or *Y* corresponds to $[1\bar{1}00]$. To obtain a direct correlation between the defect symmetry axes and the crystallographic directions, an XRD investigation of the same samples has been undertaken in the present work. From the present study the *Y* axis is found to be parallel to $[1\bar{1}00]$,

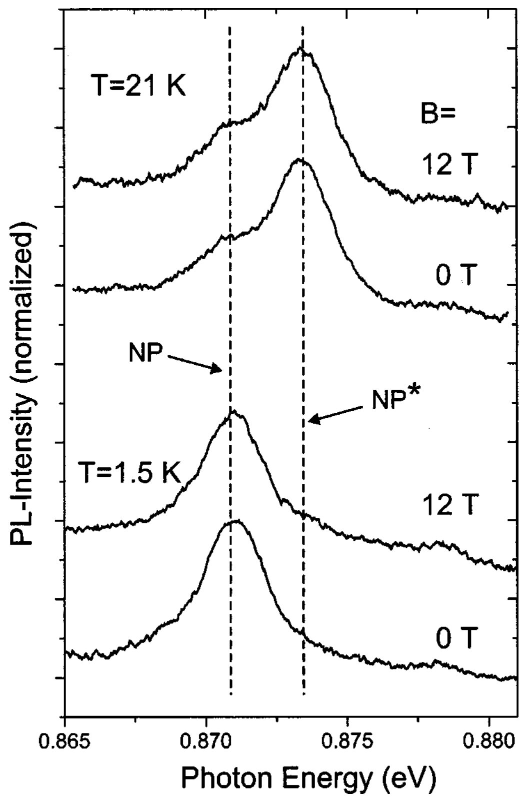

FIG. 3. Results of the Zeeman experiments. In the lower part NP is shown at 1.5 K for $B=0$ T and for a magnetic-field parallel to the c axis at $B=12$ T. In the upper part **B** is applied approximately 45° off the c axis, and the temperature is sufficiently high to make NP* the dominant emission (21 K). NP and NP* show no sign of splitting, broadening, or shift in either configuration.

where the largest splitting between the outermost ODMR lines occurs. The X axis is thus along $[11\bar{2}0]$.

A spectral dependence study of the ODMR signals both in the X band[11] and in the Q band[12] further confirmed that $L2$ is detected via the 0.88-eV PL emission, evident from the resolved phonon structure.

B. Zeeman experiments

The ODMR results presented so far suggest a direct link between the spin triplet and the monitoring of the 0.88-eV emission. An obvious choice for the spin triplet would be the excited state of the same defect, which gives rise to the 0.88-eV PL emission. In order to confirm or discard this assignment we performed Zeeman experiments on the NP line and the hot no-phonon line NP*.[10] These PL lines can be as narrow as 1.7 meV. The measurements were performed in magnetic fields up to 12 T and at orientations of $\mathbf{B}\parallel c$ axis and at an angle of 45° between **B** and the c axis (Fig. 3). From the g value of the spin-triplet state determined by ODMR, a splitting between the $M_s=\pm 1$ sublevels at 12 T can be estimated to be approximately 2.8 meV. This is noticeably larger than the PL linewidth and should be observed if any splitting occurs. But as shown in Fig. 3 no sign of any splitting or shifting was observable for both NP and NP* at any condition. This is only consistent with the interpretation of a singlet-to-singlet transition for both NP and NP*. Therefore we can conclude that the spin triplet must be detected indirectly via the 0.88-eV emission.

C. LAC experiments

To obtain further information on the spin triplet and the 0.88-eV emission, LAC experiments were attempted. LAC occurs when two interacting magnetic sublevels approach each other at a certain magnetic field.[13] From the spin-Hamiltonian for the spin triplet the expected LAC field positions are 195 G for $\mathbf{B}\parallel c$ axis and 465 G for $\mathbf{B}\parallel[1\bar{1}00]$.

Figure 4(a) shows the results of the LAC studies when the magnetic field is along the three main crystallographic axes and at an angle of 15° between **B** and the c axis. At $\mathbf{B}\parallel c$ axis three features are resolved, one broad signal denoted as LD, LAC1 at around 310 G, and a relatively narrower signal at around 225 G (LAC2). Preliminary results of the first two signals were reported earlier.[9] In this work, we performed a complete angular dependence study and a careful analysis of the possible contributions from other overlapping emissions. We are now able to reveal the third feature LAC2, which occurs near the expected field position for the spin triplet studied in ODMR and is therefore attributed to the same triplet. In Fig. 4(b) satisfactory fits to the experimental data are shown together with the deconvolution of the various contributions. The absence of the expected LAC of the spin triplet at 465 G when **B** is along $[1\bar{1}00]$ is likely due to the fact that only one-third of the total number of inequivalent orientations allowed for the spin triplet should contribute to the LAC in this direction.

Though LD and LAC1 are not expected for the spin triplet, they are shown to be detected via the 0.88-eV PL emission as evident from their spectral dependence with resolved phonon replicas [Fig. 5(a)]. The 0.93-eV PL band can also be seen in the spectral dependence of LD and LAC1 as a negative background signal in the derivative mode, as shown in Fig. 5(a). This is due to a monotonous decrease of the PL intensity in this wavelength region with increasing field [Fig. 5(b)].

The angular dependence study showed that LD is nearly isotropic and corresponds to a monotonous decrease in the PL intensity with increasing magnetic field. Such a nonresonant feature has in the past been commonly observed as being due to other physical mechanisms such as the effect of magnetic field on wave functions of recombining carriers and also on the diffusion length of photoexcited carriers.[14] The LAC1 signal, on the other hand, represents a true LAC feature, evident from its distinct resonancelike line shape and a strong angular dependence of its intensity. The exact origin of LAC1 is still unclear.

D. Selective excitation

To shed light on the mechanism for the indirect detection of the spin triplet via the 0.88-eV emission and also to minimize the complication introduced by the strong spectral overlap between the 0.88-eV PL emission and the other emissions, selective excitation experiments were attempted with IR laser light from a Ti:sapphire laser and the Ar^{+} laser. A selective excitation of the 0.88-eV PL emission was not possible in all but only a few samples under investigation.

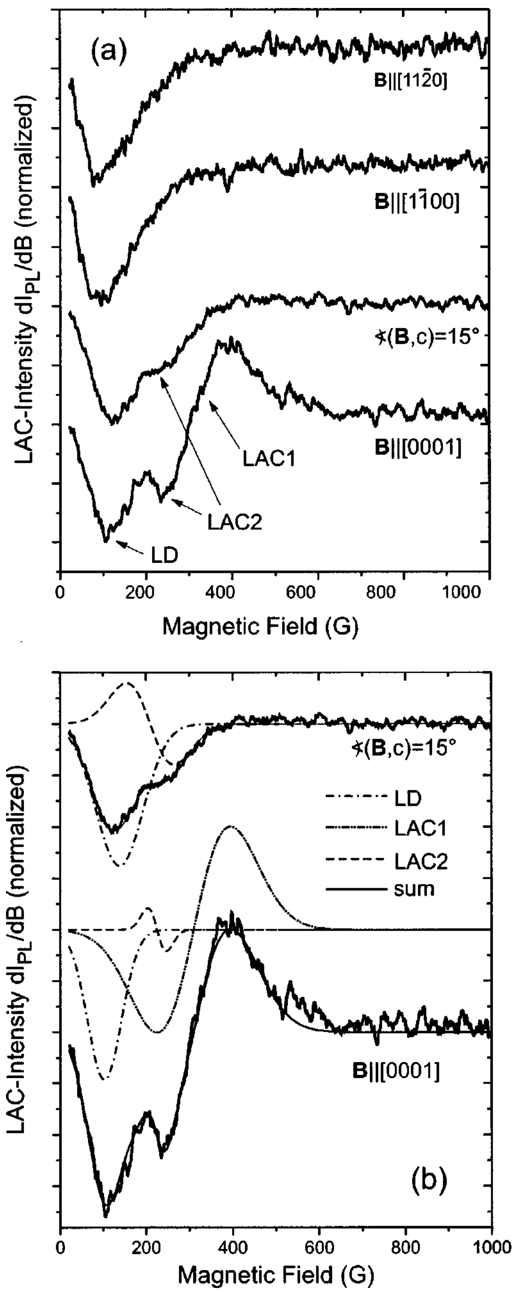

FIG. 4. (a) Level anticrossing (LAC) spectra with the magnetic field **B** oriented along the high-symmetry directions and at an angle of 15° between **B** and the *c* axis. The derivativelike shape of the lines is due to the detection mode using field modulation. Line LD is almost isotropic and can be detected at all angles. LAC1, on the other hand, is strong only in a narrow range of angles close to the *c* axis. LAC2 also decreases with increasing angle, but is observable even after LAC1 has disappeared completely at 15°. (b) Fit to the experimental data together with a deconvolution of the different contributions. When **B**‖[0001], the deduced LAC1 and LAC2 positions are 310 G and 225 G, respectively. When **B** is 15° off the *c* axis, the LAC2 field position is at 210 G with a broader linewidth as compared to that when **B**‖[0001]. The agreement between the simulated and experimental LAC spectra is satisfactory.

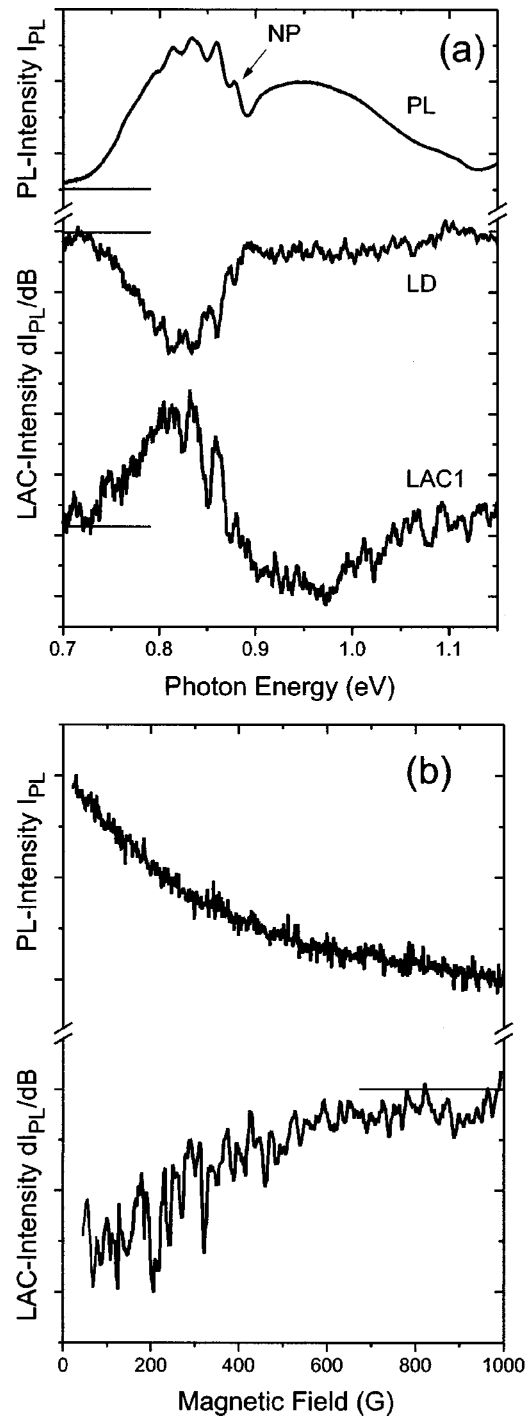

FIG. 5. (a) Spectral dependence of the LD (detected at 108 G) and LAC1 (detected at 380 G) signals, and the PL spectrum for comparison. Both signals can be detected via the 0.88-eV emission. The PL intensity of the broad band peaking at 0.93 eV decreases monotonously with increasing magnetic field, which explains its appearance in the spectral dependence of the two signals. (b) The LAC spectrum obtained by monitoring the 0.93-eV PL emission, in both the normal PL mode (upper curve) and the derivative mode (lower curve).

Apparently the Fermi level has to have a special position in the band gap so that the right charge state is reached if the experiment should be successful. When selective excitation is successful, the 0.88-eV emission is very strong while the broad background emission is very weak [Fig. 1(b)]. Nevertheless no ODMR signal was observable under this condition. Moreover, under the selective excitation of the 0.88-eV PL only LD can be detected (Fig. 6), with possibly a small

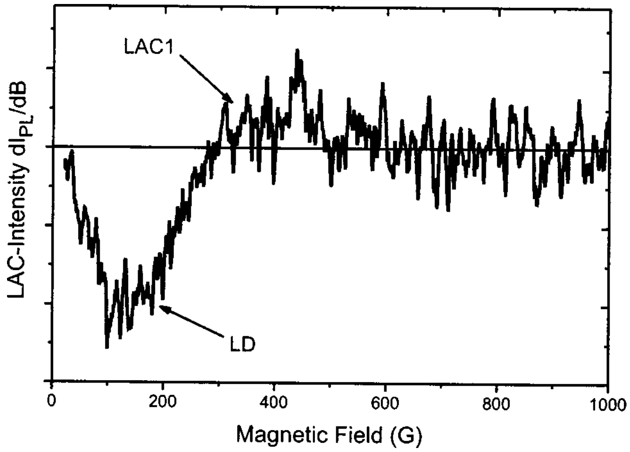

FIG. 6. The LAC spectrum under the selective excitation (photon energy 1.137-eV) for **B**∥[0001]. Of the three LAC signals only LD remains with possibly a small contribution of LAC1.

contribution of LAC1. LAC2, which is suggested to originate from the spin triplet, is unobservable.

IV. DISCUSSION

From the direct correlation between the 0.88-eV emission and the ODMR and LAC of the spin triplet presented above, it is rather tempting to suggest that the spin triplet is the excited state emitting the 0.88-eV PL. This direct link can be safely ruled out, however, based on the results from the Zeeman studies of the 0.88-eV PL emission, where both the excited and ground states have been shown to be nondegenerate singlets. This is consistent with the experimental observation under the selective excitation when the 0.88-eV PL emission could be efficiently excited but the ODMR and LAC2 signature of the spin triplet seem to be missing. This is also confirmed by the earlier studies where the somewhat indirect indication was found from a different saturation behavior between the 0.88-eV PL and the spin-triplet ODMR signal.[12] Further support can be found from the absence of the spin-triplet ODMR by monitoring the 0.88-eV PL in a partially annealed hydrogen-implanted sample.[15]

The observation of a spin-triplet ODMR via a singlet-to-singlet PL emission is not surprising, though. In fact it has been observed in semiconductors for defect systems which give rise to excited states consisting of a spin triplet and a singlet, split off by the exchange interaction.[16] The optical transition from the spin-triplet excited state to the singlet ground state is usually forbidden by the spin selection rule and cannot be seen in the PL experiments in some cases. A spin-resonance-induced transition among the triplet sublevels can, however, be observed via the singlet-to-singlet optical transition by altering the recombination rate and depopulation of the metastable triplet and thus the number of defect centers available for the optical transition.

Though no definite conclusions can be made so far, the results from the selective excitation seem to suggest that this may not be the case here. If our earlier suggestion that the excited state involved in the 0.88-eV PL is a rather shallow excited state near the conduction-band bottom is correct,[10] the 0.88-eV-PL center should be ionized by the photoexcitation process upon selective excitation. In this case, all of its

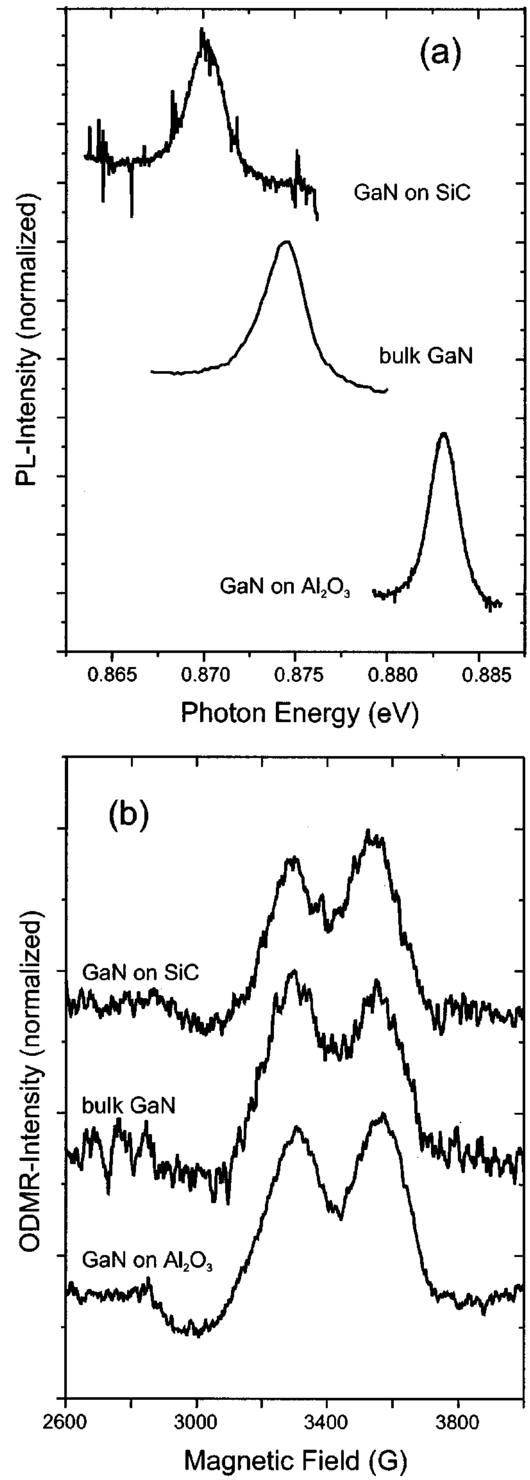

FIG. 7. (a) Spectra showing the strain effect on the energetic position of the no-phonon (NP) PL lines. The position varies from 0.870 eV for tensile-strained samples on a 6H SiC substrate to 0.883 eV for compressively strained samples on sapphire (Al_2O_3). (b) ODMR spectra of the same samples where no noticeable influence of the different strain on the ODMR line positions can be found.

excited states can be populated during the carrier recapture and recombination process. If the spin triplet was one of these excited states it should have been observed in the experiments. The failure to do so seems to suggest that the spin triplet might not be a nonradiative excited state of the same defect that gives rise to the 0.88-eV PL. In other words, the spin triplet may belong to another defect of different origin. It is also interesting to note the difference in the strain dependence of the 0.88-eV PL and the spin triplet. The energetic position of the no-phonon line in PL varies drastically from the tensile-strained GaN on SiC substrate (0.870 eV) to the compressively strained GaN on sapphire (0.883 eV) as shown in Fig. 7(a). The change in the $L2$ ODMR line positions of the same samples on the other hand is only marginal [Fig. 7(b)].

Alternative models for the observation of a spin-triplet ODMR signal via a singlet-to-singlet transition are (a) an intercenter competing recombination process of free carriers or (b) a direct intercenter feeding process. In case (a) the competing channel may also be detected via some other emissions, which have been affected by the loss of free carriers. In our experiments, no sign of the triplet ODMR could be detected in any of the samples under investigation in wavelength regions other than the one containing the 0.88-eV PL. Therefore case (a) seems to be unlikely. However, no final conclusion can be drawn at this point; further experiments are necessary to resolve this issue.

The low symmetry of the defect and the fact that the principal axis producing the largest splitting of the ODMR lines is not along the *c* axis (which is the axis of the highest symmetry in wurtzite GaN) imply that the defect is probably a complex or a lattice-distorted defect. Unfortunately no hyperfine structure is resolved in the ODMR experiments. Thus a chemical identification of the defect is not possible. However, since we can observe the signal in all electron-irradiated samples it is reasonable to assume that only intrinsic defects and common contaminants are involved.

V. SUMMARY

Detailed information on the electronic structure and recombination process related to the 0.88-eV PL emission in electron-irradiated wurtzite GaN is provided by a combination of various magneto-optical techniques. Both the excited states and the ground state involved in the 0.88-eV PL emission have been shown to be nondegenerate singlets. By monitoring the same PL emission, however, a triplet can be observed in ODMR and LAC. It arises from a spin triplet related to a defect with rhombic symmetry. Indirect recombination processes in terms of intracenter or intercenter transitions between the PL singlets and the spin triplet detected in ODMR and LAC may explain this observation.

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[1] S. Nakamura and G. Fasol, *The Blue Laser Diode* (Springer, Berlin, 1997).

[2] M. Kunzer, U. Kaufmann, K. Maier, J. Schneider, N. Herres, I. Akasaki, and H. Amano, Mater. Sci. Forum **143–147**, 87 (1994).

[3] G. D. Watkins, in *Deep Centers in Semiconductors*, 2nd ed., edited by S. T. Pantelides (Gordon and Breach, Switzerland, 1992), p. 177.

[4] M. Linde, S. J. Uftring, G. D. Watkins, V. Härle, and F. Scholz, Phys. Rev. B **55**, R10 177 (1997).

[5] G. D. Watkins, M. Linde, P. W. Mason, H. Przybylinska, C. Bozdog, S. J. Uftring, V. Härle, F. Scholz, W. J. Choyke, and G. A. Slack, in *Proceedings of the 19th International Conference on Defects in Semiconductors, Aveiro, 1997*, edited by G. Davies and M. H. Nazaré, Mater. Sci. Forum **258–263** (Trans Tech, Switzerland, 1998), p. 881.

[6] Z. Q. Fang, J. W. Hemsky, D. C. Look, M. P. Mack, R. J. Molnar, and G. D. Via, in *Proceedings of the Nitride Semiconductors Symposium, Boston, MA, 1997*, edited by F. A. Ponce, S. P. DenBaars, B. K. Meyer, S. Nakamura, and S. Strite, (Material Research Society, Warrendale, PA, 1998), p. 881.

[7] W. M. Chen, I. A. Buyanova, Mt. Wagner, B. Monemar, J. L. Lindström, H. Amano, and I. Akasaki, Phys. Rev. B **58**, R13 351 (1998).

[8] I. A. Buyanova, Mt. Wagner, W. M. Chen, B. Monemar, J. L. Lindström, H. Amano, and I. Akasaki, Appl. Phys. Lett. **73**, 2968 (1998).

[9] I. A. Buyanova, M. Wagner, W. M. Chen, L. Lindström, B. Monemar, H. Amano, and I. Akasaki, MRS Internet J. Nitride Semicond. Res. **3**, Article 18 (1998).

[10] I. A. Buyanova, Mt. Wagner, W. M. Chen, N. V. Edwards, B. Monemar, J. L. Lindström, M. D. Bremser, R. F. Davis, H. Amano, and I. Akasaki, Phys. Rev. B **60**, 1746 (1999).

[11] Mt. Wagner, I. A. Buyanova, W. M. Chen, B. Monemar, J. L. Lindström, H. Amano, and I. Akasaki, in *Proceedings of the 24th International Conference on the Physics of Semiconductors, Jerusalem, 1998*, edited by D. Gershoni (World Scientific, Singapore, 1999), Article IX B 3.

[12] C. Bozdog, H. Przybylinska, G. D. Watkins, V. Härle, F. Scholz, M. Mayer, M. Kamp, R. J. Molnar, A. E. Wickenden, D. D. Koleske, and R. L. Henry, Phys. Rev. B **59**, 12 479 (1999).

[13] W. M. Chen, M. Godlewski, B. Monemar, and J. P. Bergman, Phys. Rev. B **41**, 5746 (1990).

[14] W. M. Chen, O. O. Awadelkarim, H. Weman, and B. Monemar, Phys. Rev. B **42**, 5120 (1990).

[15] M. G. Weinstein, M. Stavola, C. Y. Song, C. Bozdog, H. Przbylinska, G. D. Watkins, S. J. Pearton, and R. G. Wilson, MRS Internet J. Nitride Semicond. Res. **4S1**, Article G5.9 (1999).

[16] K. M. Lee, K. P. O'Donnell, J. Weber, B. C. Cavenett, and G. D. Watkins, Phys. Rev. Lett. **48**, 37 (1982).