Fine Structure of Effective Mass Acceptors in Gallium Nitride

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Magnetoluminescence of the exciton bound to a neutral acceptor was measured to investigate the electronic structure of a shallow acceptor center in GaN. The application of magnetic fields along different directions with respect to the crystal c axis allowed us to determine the symmetry of the ground (Γ_9) and the first excited state (Γ_7) of the acceptor. The observed Zeeman splitting pattern has axial symmetry but can be explained well only by assuming a significant reduction of the spin-orbit interaction for this acceptor state. Because of this reduction, the energy structure of the neutral acceptor is found to be very sensitive to any local, axial perturbation.

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The precise control of doping, which is essential for appropriate device design, continues to stimulate the basic studies of impurity centers in semiconductors. There is a rekindled interest in wide gap compounds of which gallium nitride (GaN) is a relevant example. This material has already been implemented in operating devices [1], and many new applications are foreseen [2]. As in other semiconductors, donor centers in GaN are relatively well understood while the physics of acceptor states is far from being clear. The low symmetry of the wurtzite crystal lattice of GaN implies a characteristic anisotropy of the valence-band states. A magnetic field $\mathbf{B}$ applied along the wurzite $\mathbf{c}$ axis is expected to split the ground Γ_9 valence-band doublet, while no splitting should occur if $\mathbf{B} \perp \mathbf{c}$. This characteristic anisotropy of the valence band is confirmed in studies of free excitons [3]; however, the valence-band holes localized on acceptor states show very weak anisotropy when, for example, studied in EPR experiments [4].

In this Letter, we clarify the controversy concerning the symmetry of acceptor states in gallium nitride by studying the angle-resolved magnetoluminescence of excitons bound to neutral acceptors in samples with low doping concentrations. The samples chosen and the applied experimental technique allow us to probe well-isolated acceptor states, which indeed are found to reflect the symmetry of the valence band. However, the experimental data are only well reproduced in calculations if a large reduction of the spin-orbit interaction for a hole localized on an acceptor as compared to the free hole is assumed. The effects of the spin-orbit interaction, small for isolated acceptors, are very likely not visible in experiments on samples with high (intentional) doping concentrations and therefore with acceptor centers which suffer additional local symmetry effects [5] caused, for instance, by the presence of neighboring impurities. A precise analysis of the symmetry of the isolated acceptor state based on our experiments is feasible due to the unique possibility of observing the A^0X luminescence involving not only the lowest energy Γ_9 acceptor doublet but also the higher Γ_7 doublet. The reported magnitude of the reduction of the spin-orbit interaction cannot be explained by the conventional effective mass theory applied to acceptor states [6]. Similar effects are also found for other materials such as diamond [7,8] or even silicon [9,10]. The advanced calculations predict a fractional reduction of the spin-orbit interaction for deep acceptor centers [9] but, even then, the quantitative agreement is far from being satisfactory. This problem remains controversial [11], and visibly requires further theoretical work. A large reduction of the spin-orbit coupling for an acceptor bound hole as compared to the free one has significant consequences on spectroscopic properties of acceptors in a large class of wurzite-symmetry semiconductors. We demonstrate here that the interplay between the actual strength of the spin-orbit interaction for an isolated acceptor and the effects of local axial fields present in heavily doped materials is the reason why, depending on the experimental probe and samples used for investigations, the acceptor centers hardly ever reflect the valence-band anisotropy in wurzite-symmetry semiconductors [4,12,13].

The samples used for investigations were intentionally undoped, homoepitaxial GaN layers grown by metal-organic chemical-vapor deposition on GaN bulk crystals along the wurtzite c axis. In the experiments, we have measured the low temperature (helium bath), near band-edge luminescence spectra in magnetic fields up to 25 T, for different orientations of the magnetic field with respect to the crystal c axis. More on experimental details can be found in Ref. [14]. As illustrated in the inset of Fig. 1, the typical near band-edge emission spectrum of our samples [14] shows distinct transitions related to both the exciton bound to a neutral donor (D^0X) and the exciton bound to a neutral acceptor (A^0X), as well as a weak feature related to the free exciton (X_A). Here

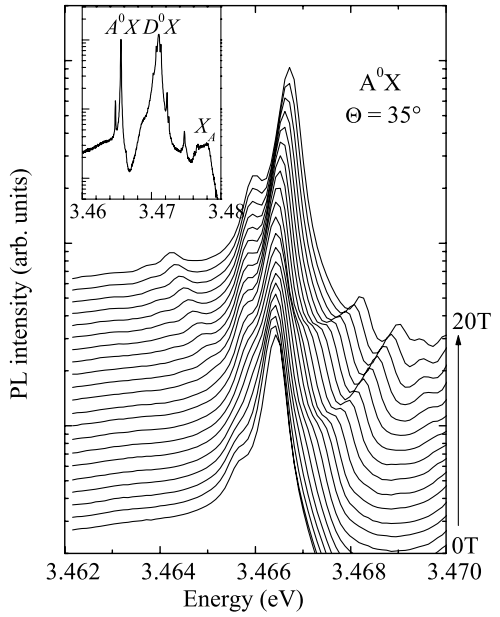

FIG. 1. Photoluminescence spectra of the exciton bound to a neutral acceptor (A^0X) in GaN recorded at different values of magnetic field oriented at 35° to the c axis. Inset: Photoluminescence spectrum of GaN in the range of excitonic transitions.

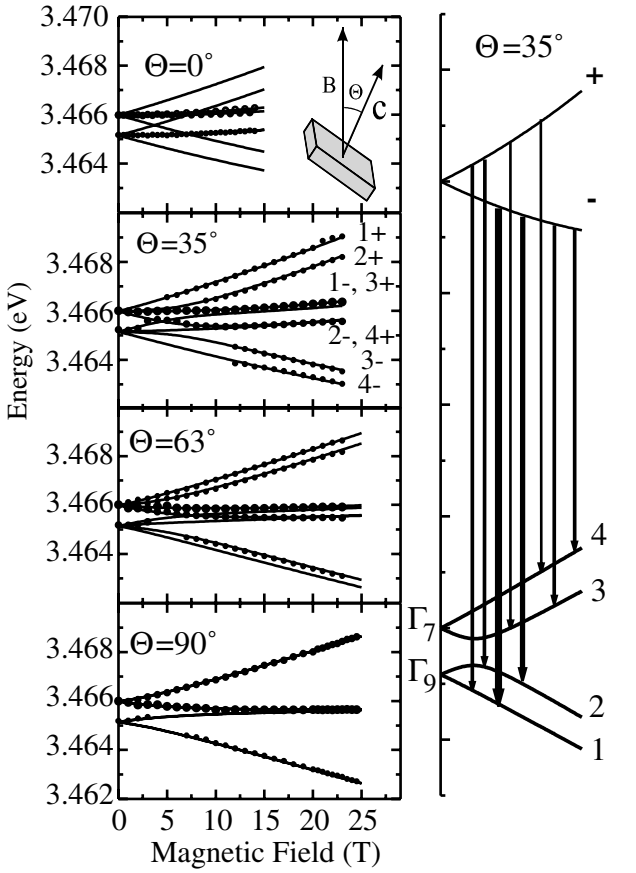

FIG. 2. Left side: points: energies of the Zeeman components of the A^0X recombination, as a function of the magnetic field, measured for different orientations of **B** with respect to the c axis of the sample; solid lines: calculated results according to the proposed model. Right side: schematic presentation of the initial and final states involved in the A^0X recombination for $\Theta = 35°$.

we concentrate on the A^0X emission, which, as previously discussed [14] shows, at zero magnetic field, a characteristic doublet structure with a dominant transition on the high energy side and less intense low energy satellite (0.8 meV below the dominant line). The sample-independent intensity ratio between both components of the A^0X doublet is an indication that this doublet structure is the property of the recombination related to a single impurity center [14]. The doublet character of the A^0X recombination is found to be due to the ground as well as the first excited acceptor levels being involved in the final state of the recombination process considered.

Representative traces of the A^0X luminescence, measured as a function of the magnetic field applied along a direction tilted from the c axis by $\Theta = 35°$ are shown in Fig. 1. The field evolution, and, in particular, the observed Zeeman pattern of the A^0X doublet, is remarkably anisotropic. This can be clearly seen in Fig. 2, where the energies of the observed magnetoluminescence peaks are plotted for four different angles Θ. For the $\Theta = 0°$ configuration, only four central, circularly polarized lines are observed [14]. At $\Theta \neq 0$, additional doublets [marked by $(1+, 2+)$ and $(3-, 4-)$ in Fig. 2], forbidden at $\Theta = 0°$, appear at energies higher and lower with respect to the central components. These "forbidden" doublets gain in intensity upon increasing Θ, but at the same time the splitting between the doublets' components becomes smaller and smaller.

In the following, we distinguish between the initial and final state involved in the A^0X luminescence. The initial state is a three particle complex (one conduction band electron and two holes) bound to an acceptor potential. In the final state, we are left with a single hole on the acceptor potential, i.e., with a neutral acceptor state A^0. In spite of its possible complexity, the initial state can be supposed to react to a magnetic field as if it were a single electron (weakly) bound state (two holes with opposite angular momentum $j_z = \pm 3/2$ are paired off). We follow such a simple model [15] assuming that the energies $E^{\pm}$ of the Zeeman components of the initial state (measured with respect to the reference energy $E_{A^0X} =$ 3.466 eV set to be equal to the energy of the main A^0X line at zero magnetic field) are given by

$$E^{\pm} - E_{A^0X} = \pm\tfrac{1}{2} g_{A^0X} \mu_B B + d_{A^0X} B^2. \qquad (1)$$

Nevertheless, we account phenomenologically for the possible complexity of the initial state by allowing the effective g factor g_{A^0X} and the diamagnetic coefficient d_{A^0X} to be anisotropic (i.e., Θ dependent).

It is now possible to extract the properties of the initial state involved in the A^0X luminescence (i.e., to establish

the anisotropy of the g_{A^0X} and d_{A^0X} coefficients). This can be done without referring to the detailed calculations of final states but only under some general assumptions regarding these states. As can be seen in Fig. 2 (right panel), we consider that at zero magnetic field the final state involved in the A^0X luminescence is a two-level (each twofold degenerate) state. When the magnetic field is applied and the spin degeneracy lifted, the A^0X recombination involves the two-level initial state and the four-level final state. We expect up to eight transitions to be visible in the magnetoluminescence spectra, the exact number of the observed transitions depending, however, on the selection rules and coincidental degeneracy, both being determined by the field configuration. Nevertheless, for a given $\Theta \neq 0$ configuration, we may easily distinguish the characteristic pairs of transitions, e.g., the pairs $(1+, 1-)$, or $(2+, 2-)$, shown in Fig. 2. The two transitions within such a pair involve the same final state but originate from different initial states. The energy difference between these transitions provides the energy splitting of the initial state and allows a direct evaluation of g_{A^0X} for each value of $\Theta \neq 0$ (and extrapolation of g_{A^0X} for the $\Theta = 0$ case). Further, we suppose that the effect of the diamagnetic shift of the observed transitions is entirely due to the initial state. This seems to be logical since the mean radius of the electron in the A^0X complex is significantly larger than that of the hole localized on the acceptor. For each Θ, we can now extract the field dependence of the mean energy of the observed transitions and estimate the Θ dependence of the diamagnetic coefficient d_{A^0}. This estimation of the d_{A^0} parameter can be then readjusted *a posteriori*, after reproducing the final state in detailed calculations which do not include terms quadratic with the magnetic field and therefore imply that the mean energy of the four final-state components is independent of the magnetic field. The sensitivity of the initial state parameters to the field configuration is illustrated in Fig. 3.

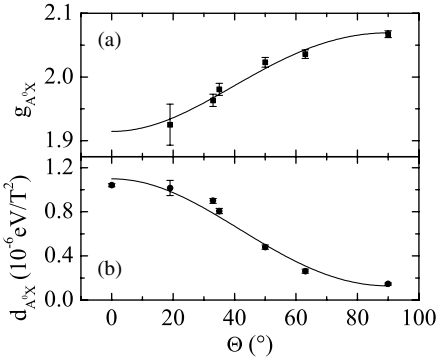

FIG. 3. Variation of the effective g factor g_{A^0X} and the diamagnetic shift d_{A^0X} of the ground state of the A^0X complex, as a function of the angle between **B** and the c axis of the sample. Points: values derived from the experimental data; solid lines: guides to the eye. When $\Theta = 0$, the extrapolated value of $g_{A^0X} = 1.914$.

Having established the parameters of the initial state, we can now reconstruct the final-state neutral acceptor levels (see Fig. 4) by subtracting the energies given by Eq. (1) (with known d_{A^0} and g_{A^0X} for each angle Θ) from the measured transition energies [the extrapolated value $g_{A^0X} = 1.914$ has been used for the case of $\Theta = 0$; see Fig. 3(a)]. A conventional model [15] of the A^0X luminescence, which accounts only for the Γ_9 ground acceptor states in the final state, is not sufficient to interpret our results. Here, we observe that the first excited state of the neutral acceptor also contributes to the luminescence. It is doubly degenerate at zero magnetic field, similarly to the ground state. When **B** is applied parallel to the c axis, both the ground and first excited state doublets split in a similar way. The **B** component perpendicular to the c axis introduces an interaction between them (Fig. 4). To explain such a behavior, we propose to use a simplified description of the acceptor states, based on group theory. We assume that the Coulomb energy plays the dominant role and limit our considerations to the sixfold degenerate ground state of $1s$ symmetry, which can be described using the $|l_z, s\rangle$ basis. The quantum numbers correspond to the orbital ($l_z = 1, 0, -1$) and spin momenta of the hole ($s = \pm 1/2$) with the z direction parallel to the c axis. For crystals with the wurtzite symmetry, the sixfold degeneracy is lifted and, within a quasicubic approximation, the resulting energies are given by the Hamiltonian,

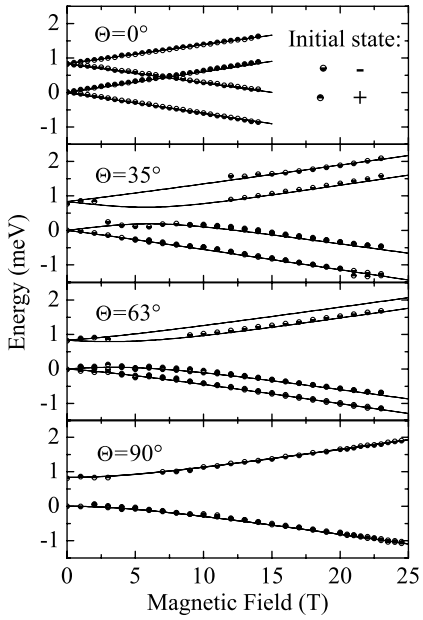

FIG. 4. Energies of the Zeeman components of the ground and first excited state doublets of the neutral acceptor in GaN as a function of the magnetic field, for different orientations of **B** with respect to the c axis of the sample. The upper (lower) half-filled points were obtained through recalculation from the transition energies related to + (−) Zeeman components of the initial A^0X ground state. A full point is seen when such two results coincide. Solid lines: results of calculations [Eqs. (2) and (3)].

$$H_0 = E_c - \Delta'_{cf} l_z^2 - \tfrac{2}{3}\Delta'_{so}\mathbf{l}\cdot\mathbf{s}, \quad (2)$$

where E_c is the Coulomb energy and the two parameters Δ'_{so} and Δ'_{cf} describe the spin-orbit and crystal-field interactions, respectively. These two parameters can have different values than those used to describe the (valence) band states since they depend on the localization extent of the hole wave function [6]. The linear effect of the magnetic field for the neutral acceptor can be included as follows:

$$H_B = g_0\mu_B\mathbf{B}\cdot\mathbf{s} + g_1\mu_B\mathbf{B}\cdot\mathbf{l}, \quad (3)$$

where μ_B is the Bohr magneton, and g_0 and g_1 are the g factors for the spin and orbital angular momenta, respectively.

Using the Hamiltonian $H = H_0 + H_B$, we can reproduce the results displayed in Fig. 4, assuming, however, a strong reduction of the spin-orbit interaction for the hole bound at the neutral acceptor. A least squares fit (Fig. 4) provides the value $\Delta'_{so} = 1.30(2)$ meV as compared to $\Delta_{so} = 18.1$ meV deduced from studies of free excitons [3]. It is found that Δ'_{cf} has to be significantly larger than Δ'_{so}, but our experiment is not sensitive to its particular value. In calculations, we have therefore used the value appropriate for the free exciton $\Delta_{cf} = 10.2$ meV [3]. We assume $g_0 = 2.003$ as for the free electron and find $g_1 = 0.041(5)$. The calculations show that the neutral acceptor ground state is of Γ_9 symmetry with $|+1, +1/2\rangle$ and $|-1, -1/2\rangle$ states, while the first excited state doublet is of Γ_7 symmetry with almost pure $|+1, -1/2\rangle$ and $|-1, +1/2\rangle$ states.

The small separation between the ground and the first excited state of the neutral acceptor makes its energy structure extremely sensitive to local axial fields in directions not aligned with the wurtzite c axis. Such a perturbation can be simulated by adding a term $\Delta_{ax}(l_x^2 - l_y^2)$ to the Hamiltonian given by Eq. (2). It has been verified that, for Δ_{ax} of the order of 1 meV, the symmetry of the acceptor states is significantly modified, implying an effective quenching of orbital momentum effects [5]. As a consequence, the Zeeman splitting of such a perturbed center is almost spherical, as observed in EPR and optically detected magnetic resonance experiments [4].

We now turn back to the initial state of the A^0X recombination, and comment on its anisotropy expressed in terms of the Θ dependence of the effective parameters g_{A^0X} and d_{A^0X} (see Fig. 3). Simple reasoning predicts that the A^0X initial state should reflect the properties of the conduction band electron which, on the other hand, is known to be rather isotropic in GaN [4]. The reason for the observed anisotropy is that in our case the properties of the three particle A^0X complex are far beyond those of a single electron state. Although the detailed description of our calculations of the energy levels of the A^0X complex is beyond the scope of this paper, we can quantitatively reproduce the effects of anisotropy shown in Fig. 3 using a set of sensible parameters. (As expected, we find that the hole involved in the A^0X complex resembles the one of the free exciton but is very different from that localized on the acceptor state). As a matter of fact, the lines drawn as guides for the eye in Fig. 3 overlap with the results of our calculations. These calculations show that an interaction with the excited states is responsible for the observed anisotropy of the ground state of the A^0X complex.

In conclusion, we have employed angle-resolved magnetoluminescence to study the electronic structure and symmetry of shallow acceptor states in GaN. In high quality samples, the symmetry of these states was found to reflect the symmetry of subsequent valence subbands, as expected for a conventional effective mass center. However, the hole bound to the shallow acceptor in GaN was found to suffer a large reduction of the spin-orbit interaction parameter as compared to the value expected for the valence-band states. Similar effects are observed in other semiconductors and are still awaiting a firm theoretical explanation. It has been shown that, in consequence of this reduction, the expected valence-band symmetry of acceptors in wurzite semiconductors might be broken by small axial perturbations, which explains the unexpected, but often observed, nearly isotropic acceptors in these compounds.

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