The V^{3+} center in AlN

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We investigated the magnetooptical properties of 0.9 eV luminescence in AlN. The zero-phonon lines at 0.943 eV in AlN are attributed to a transition within a d^2 configuration because of a characteristic threefold ground-state splitting in magnetic fields. We determine a g value of 1.96 ± 0.07 and a zero-field splitting of 120 ± 30 μeV for the ${}^3A_2(F)$ ground state. On the basis of the temperature dependence in a magnetic field, we attribute the 0.943 eV zero-phonon line in AlN to the ${}^1E(D) - {}^3A_2(F)$ transition of isolated V^{3+}. The different fine structures of the excited state in AlN and GaN are explained in a Tanabe–Sugano diagram. © *1997 American Institute of Physics.* [S0003-6951(97)02446-7]

Despite the enormous progress in growth and device technology there is very little information about deep defects in group III nitrides. Transition metals (TMs) form deep defects and can be expected to be common contaminations of these materials, which are grown at very high temperatures. In spite of their technological relevance for growing high resistivity material, not much detailed information on TM defects is available up to now.

Usually, the TMs are incorporated substitutionally on the metal–cation site in III–V compounds. Thus, the neighborhood of the TM is given by four nitrogen atoms. Because of the localized wave function of the deep impurity and the similar lattice constants of GaN and AlN together with their large band gaps, it is expected that internal transitions of the same transition metal element appear at about the same energy. Up to now, five TM luminescence bands have been reported for both GaN and AlN and they are discussed in Ref. 1.

On the basis of magnetooptical measurements, the electronic configurations of the 1.30 and 1.19 eV TM defects in GaN were identified. The 1.30 eV luminescence is unambiguously attributed to the ${}^4T_1(G) - {}^6A_1(S)$ transition of Fe^{3+} ($3d^5$ system),[2,3] whereas the 1.19 eV zero-phonon line (ZPL) is attributed to the ${}^1E(D) - {}^3A_2(F)$ transition of a d^2 system.[4] Ti^{2+} and Cr^{4+} have been discussed as luminescence centers.[4,5] No other magnetooptical measurements have been performed so far. For GaN, the ZPLs at 0.931 and 0.82 eV are attributed to V^{3+} (Ref. 5) or TM-complex centers.[1,6] Analogous assignments have been performed for the ZPLs at 1.297, 1.201, 1.043, 0.943, and 0.797 eV in AlN.[1] No Zeeman data have been published for AlN up to now. In this letter we report on the first Zeeman study of the 0.943 eV ZPL in AlN and compare the results with the 0.931 eV ZPL in GaN.

The AlN samples were grown by mixing Al and N at very high temperatures (1900 °C). Small AlN crystalline needles with a typical length of 3 mm and a diameter of about 100 μm were obtained. The photoluminescence (PL) was excited by various lines of an Ar^+ or Kr^+ laser. The Zeeman PL experiments were carried out using a superconducting 15 T magnet built in split-coil configuration. All Zeeman measurements were done in a Faraday configuration ($H \| k$). The luminescence was detected by a cooled Ge photodiode.

In order to investigate the fine structure of the 0.9 eV ZPLs in AlN and GaN, we performed temperature dependent PL studies. For AlN no hot lines could be detected, whereas for GaN a hot line 1.6 meV above the main peak at 0.931 eV is observed.[5] This indicates that the excited state is a singlet for AlN and a doublet for GaN. No polarization effects could be detected. High-resolution spectra of the 0.943 eV ZPL in AlN for magnetic fields of 0, 9, and 15 T are shown in Fig. 1. For 0 T, in addition to the main peak at 0.943 eV, a weak shoulder is detected on the low-energy side. These structures can be fitted with two Gaussian line shapes peaking at 0.942 55 and 0.941 70 eV. The full width at half-maximum (FWHM) is 1.5 ± 0.1 meV for the main peak and 1.9 ± 0.5 meV for the weak structure. The intensity ratio between these two peaks depends on the AlN sample.

With increasing magnetic field, a threefold splitting of the main ZPL is observed above $B = 7$ T in the configuration $H \perp c$. The intensity ratio of the three lines depends neither on the temperature nor on the magnetic field. This indicates that the splitting occurs in the ground state of the impurity. The splitting can be fitted with three Gaussian line shapes with a FWHM of 1.5 meV for each peak. It is observed that the energy splitting between the two high-energy ZPLs of the three ZPLs is slightly larger than that of the two-low energy ZPLs. This behavior indicates a zero-field splitting. The weak structure at 0.9417 eV, observed in the spectrum at 0 T exhibits a broadening up to a FWHM of 2.8 ± 0.5 meV at 15 T. Possibly this shoulder is caused by internal strain or by a disturbance in the neighborhood of the luminescence center.

The dependence of the energy positions of the three fitted peaks on the magnetic field is summarized in Fig. 2. By fitting the data points as dependent on the magnetic field, it is observed that a zero-field splitting of the ground state exists ($|D| = 120 \pm 30$ μeV). Such Zeeman behavior is a typical fingerprint for the ${}^3A_2$ ground state of a d^2 configuration in trigonal symmetry usually detected by electron paramagnetic

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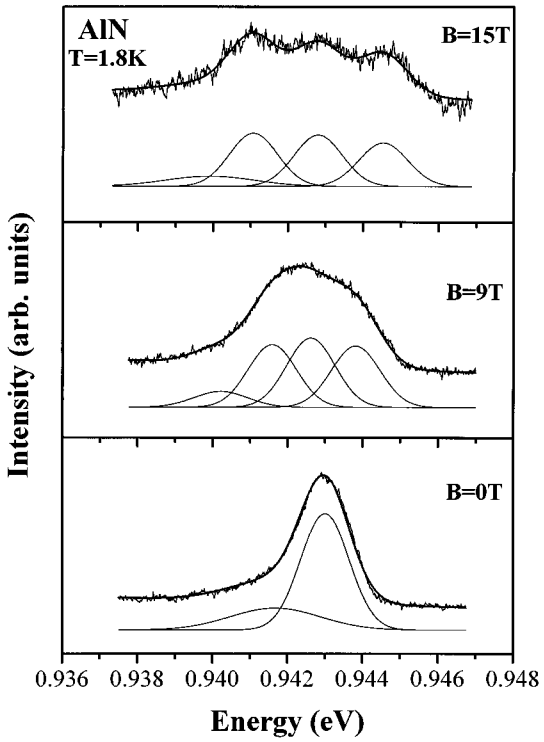

FIG. 1. Zero-phonon line region of the 0.943 eV emission in AlN for different magnetic fields at $T=1.8$ K. The threefold splitting of the main ZPL is caused by the magnetic behavior of the $^3A_2(F)$ ground state.

resonance (EPR) measurements.[7] In order to check whether the spectra are isotropic, we rotated the AlN needle at $B=14$ T from $H\perp c$ to $H\|c$. Within the margin of error, the Zeeman pattern did not depend on the rotation angle θ. Together with the almost symmetric Zeeman pattern (Fig. 2), this indicates that there is no Zeeman splitting of the excited state.

Taking into account the identical neighborhood of a TM impurity in both nitride compounds, one should expect similar ZPL energies in both compounds if these ZPLs are due to the same TM. This is what we observed in the case of the 0.943 and 0.931 eV emissions in AlN and GaN, respectively. In the context of our results, cation substitutional $V^{3+}(3d^2)$

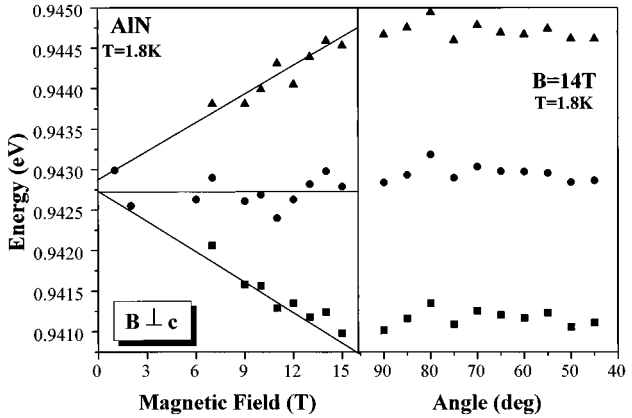

FIG. 2. Zeeman behavior of the 0.943 eV ZPL for $B\perp c$ (left) and angular dependence at $B=14$ T (right). The zero-field splitting of 120 ± 30 μeV together with the g value of 1.96 ± 0.07 are fingerprints of the $^3A_2(F)$ ground state of V^{3+}.

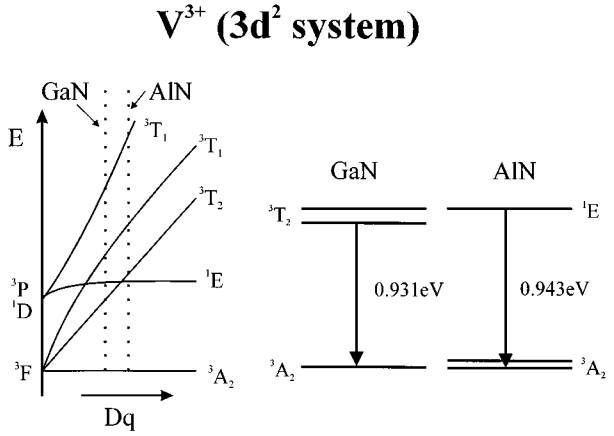

FIG. 3. Schematic Tanabe–Sugano diagram for a $3d^2$ system together with the observed fine structure for the V^{3+} center in GaN and AlN. The larger crystal-field parameter Dq for AlN is caused by the smaller lattice constant of AlN compared to that of GaN and explains the different fine structure of the excited states.

is the most probable TM candidate for these ZPLs in AlN and GaN. However, the observed fine structure of the impurity transition is slightly different for both host compounds (Fig. 3). For AlN, no hot line and no phonon sideband are observed for the 0.943 eV ZPL. Together with the isotropic threefold Zeeman splitting of the ground state it seems most reasonable to attribute this ZPL to a $^1E(D)-^3A_2(F)$ transition where the g value of the excited state is smaller than 0.1. It is expected, that the electron–phonon coupling of such a transition is small for both the ground and the excited state, explaining the missing phonon sideband. Such a weak phonon coupling is also observed for the 1.19 eV ZPL in GaN, which is caused by a $^1E(D)-^3A_2(F)$ transition.[4] As was mentioned by Baur *et al.*,[5] a hot line 1.6 meV above the main ZPL at 0.931 eV is observed for GaN. For GaAs, GaP, and InP, vanadium correlated ZPLs between 0.73 and 0.83 eV have been assigned to the symmetry forbidden $^3T_2(F)-^3A_2(F)$ crystal-field transition of V^{3+}. At higher sample temperatures hot ZPLs separated 1.2, 1.9, and 1.5 meV from the cold ZPL have been reported for these materials.[8] The analogy to the GaN PL data is obvious. The line position of the ZPL is mainly determined by the cubic crystal-field strength (Dq), which increases with the ionicity of the host crystal. Therefore, the higher energy of the emission in GaN and AlN is not suprising. The hot ZPL in GaN can be explained by a moderately strong dynamic Jahn–Teller effect:[8] The first-order spin–orbit interaction within the excited $^3T_2(F)$ state is quenched by electron–phonon coupling; thermal occupation of the upper level at elevated temperatures yields an additional hot ZPL. The splitting between the ZPLs is mainly determined by the spin–orbit coupling constant λ, which is characteristic for the incorporated impurity atom. The splitting of 1.6 meV in the GaN PL is in excellent agreement with the splittings observed for V^{3+} impurities in other III–V compounds. It is also expected that the electron–phonon coupling for the $^3T_2(F)-^3A_2(F)$ is stronger than for the $^1E(D)-^3A_2(F)$ transition, explaining the stronger phonon sideband in GaN.

The different fine structures found for GaN and AlN can be explained in the context of a schematic Tanabe–Sugano

diagram. For smaller crystal-field strength ($10Dq$), the ${}^3T_2$ state is below the ${}^1E(D)$ state (GaN case), whereas for larger crystal fields, the ${}^1E(D)$ state is below the ${}^3T_2(F)$ state (AlN case). Because of the smaller lattice constant of AlN compared to GaN, it is expected that the crystal-field strength ($10Dq$) is slightly stronger in AlN. The crystal-field transition in both cases should be located near the crossover point of the ${}^3T_2(F)$ and ${}^1E(D)$ level in the schematic Tanabe–Sugano diagram.

As mentioned above, the magnetoptical behavior (Fig. 3) of the 0.943 eV ZPL in AlN is a clear fingerprint of the ${}^1E(D)-{}^3A_2(F)$ transition. A zero-field splitting of $|D| = 120 \pm 30\ \mu$eV within the ground state is observed. In contrast to EPR, a sign of the splitting parameter D can be determined from the magnetooptical spectra. We obtain a positive sign for D and a g value of 1.96 ± 0.07. These results are in good qualitative agreement with ZnO:V^{3+}. For ZnO:V^{3+}, a ground-state g value of 1.93 and a zero-field splitting of $D = +97\ \mu$eV were obtained.[9,10] The slightly larger D value in GaN is due to the stronger covalent bonding compared to ZnO.

Similar trends for the zero-field splitting for the Fe^{3+} center in GaN compared to ZnO are also known[3] ($D = -8.84\ \mu$eV GaN, $-7.38\ \mu$eV ZnO). By comparing D for different d^2 systems in similar hosts, the spin–orbit coupling constant is the leading parameter for the magnitude of the zero-field splitting. A larger spin–orbit coupling constant λ should result in a larger D value.[7] The free-ion value of λ increases from Ti^{2+} to V^{3+} and Cr^{4+} [$\lambda = 60\ \mathrm{cm}^{-1}$ (Ti^{2+}), $106\ \mathrm{cm}^{-1}$ (V^{3+}), $163\ \mathrm{cm}^{-1}$ (Cr^{4+})] due to the larger atomic number Z. It is expected, that the zero-field splitting is similar for identical TMs in AlN and GaN. It should be emphasized, that no zero-field splitting is observed for the magnetooptical measurements of the ${}^1E(D)-{}^3A_2(F)$ transition of the 1.19 eV luminescence in GaN which was attributed to Ti^{2+} (Ref. 4) and Cr^{4+} (Ref. 5) as well. As a consequence of the missing zero-field splitting, Ti^{2+} is more likely than Cr^{4+} to explain the 1.19 eV ZPL in GaN. Observation of the zero-field splitting of the 0.943 eV ZPL in AlN is thus further proof of the V^{3+} attribution in AlN and to the 0.931 eV ZPL in GaN.

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[1] K. Pressel, R. Heitz, S. Nilsson, P. Thurian, A. Hoffmann, and B. K. Meyer, Mater. Res. Soc. Symp. Proc. **395**, 613 (1996).
[2] R. Heitz, P. Thurian, I. Loa, L. Eckey, A. Hoffmann, I. Broser, K. Pressel, B. K. Meyer, and E. N. Mokhov, Appl. Phys. Lett. **67**, 2822 (1995).
[3] K. Maier, M. Kunzer, U. Kaufmann, J. Schneider, B. Monemar, I. Akasaki, and H. Amano, Mater. Sci. Forum **143-147**, 93 (1994).
[4] R. Heitz, P. Thurian, K. Pressel, I. Loa, L. Eckey, A. Hoffmann, I. Broser, B. K. Meyer, and E. N. Mokhov, Phys. Rev. B **52**, 16 508 (1995).
[5] J. Baur, U. Kaufmann, M. Kunzer, J. Schneider, H. Amano, I. Akasaki, T. Detchprohm, and K. Hiramatsu, Mater. Sci. Forum **196-201**, 55 (1995).
[6] B. Kaufmann, A. Dörnen, V. Härle, H. Bolay, F. Scholz, and G. Pensl, Appl. Phys. Lett. **68**, 203 (1996).
[7] A. Abragam and B. Bleaney, *EPR of Transition Ions* (Oxford University Press, Oxford, 1970), p. 426 ff.
[8] G. Aszodi and U. Kaufmann, Phys. Rev. B **32**, 7108 (1985).
[9] R. Heitz, A. Hoffmann, B. Hausmann, and I. Broser, J. Lumin. **48&49**, 689 (1991).
[10] A. Hausmann and E. Blaschke, Z. Phys. **230**, 255 (1970).