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Crystal field and Zeeman splittings for energy levels of Nd$^{3+}$ in hexagonal AlN

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Abstract: The crystal-field and Zeeman splittings of the energy levels of Nd$^{3+}$ (4f$^3$) ⁴⁶⁻¹L_J in hexagonal phase AlN have been investigated. The multiplet manifolds of Nd$^{3+}$ (4f$^3$) analyzed include the ground state, ⁴I₀₋₂, and excited states ⁴I₁₋₂, ⁴I₃₋₂, ⁴I₅₋₂, ⁴I₇₋₂, ⁴S₀₋₂, ⁴S₃₋₂, ⁴G₅₋₂, and ⁴G₇₋₂. Experimental energy levels were obtained from analyses of the 12 K cathodoluminescence spectra from Nd$^{3+}$-implanted films of AlN, and from the 15 K photoluminescence excitation spectra and the site-selective combined excitation-emission spectra (CEES) recently reported for in situ Nd-doped hexagonal AlN grown by plasma-assisted molecular beam epitaxy (PA-MBE). CEES results identify a main site and two minority sites for Nd$^{3+}$ in both samples. Transition line strengths attributed to the ion in minority sites are relatively stronger in Nd:AlN than in Nd:GaN. The 15 K experimental Zeeman splitting of Nd$^{3+}$ are analyzed in the PA-MBE grown AlN samples and compared with the Zeeman splitting observed in Nd:GaN. The crystal-field and Zeeman splittings were modeled using a parametrized Hamiltonian consisting of atomic and crystal-field terms. We considered possible site distortion due to the size of the implanted Nd ion that would reduce the site symmetry from C₃ᵥ to C₃ or C₁₅. However, no significant improvement was obtained using these lower symmetry models, leading us to conclude that C₃ᵥ symmetry is a reasonable approximation for the main site Nd$^{3+}$ ions in AlN.

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OCIS codes: (260.3800) Luminescence; (260.6580) Stark effect; (020.7490) Zeeman effect.

References and links

1. Introduction

The spectroscopic properties of the trivalent rare earth (REE) ions, together with the physical and electrical properties of the semi-conducting aluminum nitride (AlN) host, have attracted the attention of many investigators interested in developing these materials as optoelectronic components for an expanding market of photonic devices [1–4]. The host material (AlN) is a wide band gap semiconductor (6.2 eV) with a separation between valence and conduction bands that allows for optical absorption and emission over a wide frequency range, making possible numerous REE sharp-line transitions observable due to the shielding of the electrons in the 4f subshell by the filled 5s and 5p shells of the rare earth ion core [5–7]. The physical properties of AlN are desirable for devices, due to the mechanical toughness of the material, which is essentially free from moisture absorption and the effects of corrosion from different chemical substances [8,9]. It is generally stoichiometric in composition (although vacancies do appear) when prepared either as films or single-crystals [10–12]. The relatively high thermal conductivity (2.85 W/cm°C) is an important physical property when operating high power/high temperature control devices, where expelling heat quickly and efficiently is a performance requirement [12].

In the present study, we investigate the crystal-field splitting and the Zeeman splitting of the energy levels of Nd3+ in the hexagonal (hunite) phase of AlN. The energy (Stark) levels of the multiplet manifolds of Nd3+(4f3), written in LS notation as 2S+1LJ, include the ground state, 3I9/2, and the excited states 4I11/2, 4I13/2, 4F3/2, 4F5/2, 2H9/2, 4F7/2, 4S9/2, 4G7/2, and 2G7/2. Some of the data that are modeled here have been reported recently by Metafé et al. [11] based on an analysis of the 15 K luminescence spectra of in situ Nd-doped AlN films grown by plasma-assisted molecular beam epitaxy (PA-MBE). Additionally, we have included experimental energy levels obtained from a analyses of unpublished cathodoluminescence (CL) spectra measured at 12 K by one of the authors (UV) for Nd-implanted AlN films grown on substrates of 6H-SiC (0001) by metal-organic chemical vapor deposition (MOCVD). Analyses of the CL spectra of Sm3+, Pr3+, Gd3+, and Tm3+ that involve similar film preparations of REE ions in the hexagonal phase of AlN have been reported previously [13–15].

2. Analysis of the spectra

In the present study, films of hexagonal AlN, grown on substrates of 6H-SiC (0001) by metal-organic chemical vapor deposition (MOCVD), were obtained from commercial sources. During implantation (fluence: 1 x 1013 ions/cm2), samples were tilted to avoid channeling by incident ions. Post-implantation annealing was carried out in a vacuum tube furnace at pressures near 106 mbar and 1100 K for 30 minutes. Implanted samples were mounted on the head of a closed-cycle helium refrigerator located inside the vacuum chamber. Excitation was provided by an Auger electron gun that provided electrons with energies between 100 eV and 5 keV and beam currents between 0.01 and 150 μA. Luminescence from the sample was passed through a quartz window and focused onto the entrance slit of a Czerny-Turner
spectrograph. The spectral output was observed by using various nitrogen-cooled detectors. Analysis of the Nd-implanted CL spectra provide confirmation for many of the energy (Stark) levels of Nd<sup>3+</sup> analyzed from the spectra of in situ Nd-doped hexagonal AlN samples grown by PA-MBE [11].

![Graph](image_url)

**Fig. 1.** The 12 K CL spectrum of transitions from \(^{4}F_{3/2}\) to \(^{4}I_{9/2}\). The strongest peaks are associated with Nd<sup>3+</sup> ions in the main “a” site.

Representative of the CL emission spectra is the 12 K spectrum shown in Fig. 1 for Stark level transitions between \(^{4}F_{3/2}\) and \(^{4}I_{9/2}\). Analysis of the strongest peaks observed in Fig. 1 leads to an energy level scheme that differs from the Stark levels previously reported for the main site of the \(^{4}I_{9/2}\) manifold [11]. Subsequent CEES measurements by one of the present authors (VD) involving emission between the same manifolds confirms the experimental splitting of the \(^{4}I_{9/2}\) and \(^{4}F_{3/2}\) in Table I(a) and the splitting of \(^{4}I_{9/2}\) in Fig. 1 for the main site. Weaker transitions observed in Fig. 1 can be traced to transitions that predict the levels listed for the minority site “b” [11]. Analysis of the present CL emission spectra, representing transitions from \(^{4}F_{3/2}\) to the \(^{4}I_{11/2}\) and \(^{4}I_{13/2}\) multiplet manifolds, results in the terminal Stark levels reported in Table I(a) (levels 6 through 18) that generally agree with the levels reported for the same manifolds given for the main or “a” site in [11]. We lack site-selective data to assign enough levels to the “b” site to perform a similar modeling analysis. Instead, we concentrate on the crystal-field modeling of the main or “a” site of Nd<sup>3+</sup> in AlN, where the number of experimental Stark levels (41) is sufficient to determine a possible site distortion. This includes all energy levels up to 17,000 cm<sup>-1</sup> for the “a” site of Nd<sup>3+</sup> in AlN except for the \(^{4}I_{15/2}\), \(^{2}H_{11/2}\) and \(^{4}F_{9/2}\) multiplet manifolds, where the CL and PLE spectra are too weak to provide an accurate analysis of the splitting.

The Nd site locations have been determined by Vetter et al. [14], using experimental emission channeling methods with ion-implanted \(^{14}Pm<sup>3+</sup>\) in AlN as a short-lived weak beta decay lattice site probe. The results indicated that \(^{56}(6)%\) \(^{147}Nd<sup>3+</sup>\) occupied Al sites by substitution with the remainder located in other sites, including nitrogen vacancies or interstitial sites in the lattice. Annealing the samples to temperatures of 873 K and 1373 K yield fractions of \(^{58}(5)%\) and \(^{56}(7)%\) of the \(^{14}Nd\) ions in Al sites by substitution. The lattice
location of $^{147}$Pm was also determined by monitoring the K electrons of Pm in the same decay and found to be $58(8)$% (873 K) and $44(6)$% (1373 K). These results suggest that Nd competes effectively for different vacancy sites in the lattice, but that the majority of Nd ions appear to occupy the vacant Al site. It also appears that some Nd ions complex with nitrogen vacancies in the basal plane nearest the substituted Nd. In doing so the Nd ion shifts along an axis away from the higher $C_{3v}$ symmetry site to a site such as $C_{1h}$, thus producing for these ions a lower symmetry that accounts for the observed multi-site spectra observed in both Nd:AlN [11] and Nd:GaN [16]. The minority site spectra are relatively stronger in the AlN host. We conclude that the main site or “a” site refers to Nd$^{3+}$ in Al$^{3+}$ sites in the lattice. Given the relative size of Nd to Al and the vacancies in the lattice, distortion of the ligand configuration with respect to the undoped site is expected. Thus, we modeled the crystal field splitting considering symmetry reduction from $C_{3v}$ to either $C_{3}$ or $C_{1h}$ symmetry in order to ascertain the sensitivity of the data to the symmetry.

To investigate the site symmetry, we performed descent in symmetry calculations from $C_{3v}$ to $C_{3}$ (assuming the mirror plane symmetry is broken) and from $C_{3v}$ to $C_{1h}$ (assuming the mirror plane symmetry remains, but the three-fold rotation axis symmetry is broken). Even though the number of independent crystal-field parameters increases from 6 (in $C_{3v}$ symmetry) to 8 (in $C_{3}$ symmetry) and 14 (in $C_{1h}$ symmetry), no significant improvement in the standard deviation of the energy-level fitting is achieved with the inclusion of these additional parameters. In $C_{1h}$ symmetry, the crystal field splitting of the $^4F_{3/2}$ manifold is improved, but there is no significant improvement in the splitting of the other manifolds, including $^4I_{9/2}$, relative to the modeling results obtained assuming $C_{3v}$ symmetry. Additionally, the calculations using $C_{3v}$ symmetry predict magnetic field splittings that are in better agreement with experiment than calculations assuming $C_{1h}$ symmetry. For that reason, the final modeling results reported below assume that the Nd$^{3+}$ ions occupy the main site of $C_{3v}$ symmetry. Experimental and calculated energy levels for all Stark levels up to 17,000 cm$^{-1}$ are listed in Tables 1(a) and 1(b). Atomic and crystal-field parameters determined from the energy level fitting (Table 2) are used to determine the wave functions for Zeeman splitting and g-factor calculations.

3. Analysis of the Zeeman splitting

The Zeeman spectra were obtained at 15 K from the PA-MBE samples in magnetic fields up to 6 T. We made use of combined excitation emission spectroscopy (CEES) to differentiate between the magnetic field splitting of Stark levels of Nd$^{3+}$ in the main (“a”) site (Tables 1(a) and 1(b) of this work) and the minority (“b”) site as labeled in [11]. As an example, we considered the emission spectrum obtained by exciting the multiplet manifolds $^4G_{5/2}$ (620 nm) and $^2D_{7/2}$ (604 nm), and detecting the emission spectra from $^4F_{3/2}$ to the ground-state manifold $^4I_{9/2}$ (930 nm). The excitation, non-radiative relaxation, and subsequent emission follow separate site-distinctive channels for Nd$^{3+}$ in the majority and minority sites. The Stark levels of the manifolds involved in this sequence, namely: $^4G_{5/2}$, $^2D_{7/2}$, $^4F_{3/2}$, and $^4I_{9/2}$, and the energies associated with each site, along with the magnetic field splitting of individual Stark levels, are listed in Table 3. Unfortunately, the magnetic field splitting is large enough to measure with reasonable accuracy for only a limited number of states. These splittings correspond to g-factors greater than one and correspond to transitions in which only one of the involved levels has a significant splitting. In a majority of cases, the magnetic field splittings are smaller than previously observed for the same transitions in Nd:GaN. Moreover, the splittings are more difficult to resolve, due to the pronounced inhomogeneous broadening of the lines, as observed in the zero magnetic field spectra. These unresolved splittings correspond to g-factors smaller than about 0.5. Magnetic fields were applied parallel and perpendicular to the crystal-growth axis and compared to the spectrum in zero magnetic field.
Figure 2 shows an excerpt of our CEES data obtained for a sample at $T = 15$ K in a magnetic field of 6 T. The format of the figure, as well as the labels representing the transitions, correspond to the figure presented earlier in an analysis of the Zeeman spectra of hexagonal Nd$^{3+}$ in GaN [16]. The upper third of the present figure shows the data in zero magnetic field with excitation photon energy between 2.016 eV and 2.028 eV. Transitions from left to right are identified as $E$, an excitation transition, and $A$, $B$, $C$, and $D$, emission transitions with “a” and “b” sites identified with the appropriate transition. In the middle part of the figure, representing the sample parallel to the c-axis in a magnetic field of 6 T, we see the splitting of these transitions. The observed splittings of transitions associated with the “a” or main site resemble the Zeeman spectra taken in the same orientation for Nd$^{3+}$ in GaN [16]. For Nd$^{3+}$ occupying the “a” site, we find that transition $A$ does not split in this geometry, but transitions $C$ and $D$ do. Following the arguments made earlier [16] we conclude that the splitting of $C$ and $D$ is dominated by the ground state. In contrast to the splitting of $C$ and $D$, and $E$ for parallel fields, the most pronounced splittings are observed for $A$ and $B$ in perpendicular fields, as shown in the lower part of Fig. 2.

Assuming Nd$^{3+}$ sites are approximated by $C_{3v}$ symmetry, the Stark levels listed in Tables 1(a) and 1(b) and Table 3 are labeled either $\Gamma_{1/2}$ or $\Gamma_{3/2}$. In this symmetry, all levels will split along the c-axis in a magnetic field. However, in a perpendicular field, only the Stark levels labeled $\Gamma_{1/2}$ will split. In principle, symmetry assignments can be made to Stark levels based on observed magnetic field splittings in the latter orientation [16]. The irreducible representations (irreps) $\Gamma_{1/2}$ and $\Gamma_{3/2}$ describing the symmetry of the wavefunction can be used interchangeably with the quantum number labels $\mu = \pm 1/2$ or $\mu = \pm 3/2$, respectively. The Stark levels assigned in Tables 1(a) and 1(b), column 3, and Table 3, column 3, are based on
the crystal-field splitting calculation with the smallest rms deviation that has calculated Zeeman splittings consistent with the observed values. The ordering of the quantum labels in Table 3 are the same as those reported for Nd:GaN, with the exception of levels (4,5) and (54,55), which are reversed [16].

![Diagram](image)

**Fig. 3.** Splitting of the ground state of Nd$^{3+}$ in the “a” and “b” sites of AlN compared with Nd:GaN; Zeeman spectra of all three sites were obtained at 6 T and 15 K with the sample parallel to the magnetic field.

In Fig. 3, the observed splitting of the ground state of Nd$^{3+}$ is compared in the AlN and GaN host. The Zeeman spectra were obtained at 6 T and 15 K for the sample parallel to the magnetic field. Three sites are involved: the AlN site “a” or main site has a splitting of 1.3 meV (10.5 cm$^{-1}$), site “b” has a splitting of 1.6 meV (12.9 cm$^{-1}$), and the splitting in the “a” site in GaN is 1.4 meV (11.3 cm$^{-1}$) [16]. The splittings for both sites in AlN can also be observed in Fig. 2. We note that the splitting in the “a” site is somewhat smaller in AlN than in GaN, but the splitting in the AlN “b” site is larger and the transitions involved are inhomogeneously broadened more than the transitions in the “a” sites.

4. Crystal-field modeling studies

The 41 experimental Stark levels of Nd$^{3+}$ in the main “a” site modeled in the present study are reported in Tables 1(a) and 1(b) for multiplet manifolds $^4I_{9/2}, ^4I_{15/2}, ^4I_{13/2}, ^4F_{3/2}, ^4F_{3/2}, ^2H_{9/2}, ^4F_{7/2}, ^4S_{3/2}, ^4G_{7/2}$, and $^6G_{7/2}$. We have an insufficient number of Stark levels identified with Nd$^{3+}$ in the minority “b” site to carry out a crystal-field site study analysis for these levels. A parameterized Hamiltonian defined to operate within the entire 4$f^8$ electronic configuration assuming that Nd$^{3+}$ ions occupy sites of C$_3$, symmetry in the “a” site was used to calculate the energy (Stark) levels. The model Hamiltonian is usually written in a form [7,17,18] that includes spherically symmetric “atomic” contributions, given by,
\begin{table}
\centering
\caption{Crystal-field splitting for energy levels of Nd\textsuperscript{3+}:AlN (part 1)}
\label{tab:crystal_field_splitting}
\begin{tabular}{llllllll}
\hline
\textsuperscript{2S + 1}L\textsubscript{j}\textsuperscript{m} & Doublet Level & Irep (\Gamma) & \textit{M}\textsubscript{l}\textsuperscript{m} & \textit{E}\textsubscript{rep} (cm\textsuperscript{-1}) & \textit{E}\textsubscript{dip} (cm\textsuperscript{-1}) & \Delta\textit{E} (cm\textsuperscript{-1}) \\
\hline
\textsuperscript{4}I\textsubscript{6/2} & 1 & 3/2 & \pm 9/2 & 0 & -6 & 6 & \sigma = 10.1^{b} \\
 & 2 & 1/2 & \pm 1/2 & 150 & 129 & 21 & \\
 & 3 & 1/2 & \pm 5/2 & 226 & 228 & -2 & \\
 & 4 & 3/2 & \pm 3/2 & 298 & 294 & 4 & \\
 & 5 & 1/2 & \pm 7/2 & 405 & 410 & -5 & \\
\textsuperscript{4}I\textsubscript{11/2} & 6 & 1/2 & \pm 11/2 & 1908 & 1916 & -8 & \\
 & 7 & 1/2 & \pm 1/2 & 1948 & 1961 & -13 & \\
 & 9 & 1/2 & \pm 5/2 & 2064 & 2073 & -9 & \\
 & 10 & 1/2 & \pm 7/2 & 2130 & 2130 & 0 & \\
 & 11 & 3/2 & \pm 9/2 & 2140 & 2140 & 0 & \sigma = 9.5 \\
\textsuperspace{\textsuperscript{4}I}\textsubscript{15/2} & 12 & 1/2 & \pm 13/2 & 3868 & 3860 & 8 & \\
 & 13 & 1/2 & \pm 1/2 & 3926 & 3928 & -2 & \\
 & 14 & 3/2 & \pm 3/2 & 3953 & 3943 & 10 & \\
 & 15 & 1/2 & \pm 5/2 & 3965 & 3965 & 0 & \\
 & 16 & 1/2 & \pm 7/2 & 4090 & 4094 & -4 & \\
 & 17 & 3/2 & \pm 9/2 & 4129 & 4121 & 8 & \\
 & 18 & 1/2 & \pm 11/2 & 4146 & 4143 & 3 & \sigma = 6.0 \\
\textsuperspace{\textsuperscript{4}T}\textsubscript{15/2} & 19 & 3/2 & \pm 15/2 & 5859 & & & \\
 & 20 & 1/2 & \pm 5/2 & 5949 & & & \\
 & 21 & 1/2 & \pm 1/2 & 6020 & & & \\
 & 22 & 3/2 & \pm 3/2 & 6023 & & & \\
 & 23 & 1/2 & \pm 13/2 & 6112 & & & \\
 & 24 & 1/2 & \pm 11/2 & 6301 & & & \\
 & 25 & 3/2 & \pm 9/2 & 6305 & & & \\
 & 26 & 1/2 & \pm 7/2 & 6341 & & & \\
\textsuperspace{\textsuperscript{4}T}\textsubscript{3/2} & 27 & 1/2 & \pm 1/2 & 10935 & 10952 & -17 & \\
 & 28 & 3/2 & \pm 3/2 & 10976 & 10965 & 11 & \sigma = 14.6 \\
\textsuperspace{\textsuperscript{3}T}\textsubscript{15/2} & 29 & 3/2 & \pm 3/2 & 11917 & 11912 & 5 & \\
 & 30 & 1/2 & \pm 5/2 & 11941 & 11942 & -1 & \\
 & 31 & 1/2 & \pm 1/2 & 12036 & 12043 & -7 & \sigma = 5.1 \\
\textsuperspace{\textsuperscript{3}H(2)}\textsubscript{15/2} & 32 & 1/2 & \pm 7/2 & 12058 & 12049 & 9 & \\
 & 33 & 3/2 & \pm 3/2 & 12070 & 12067 & 3 & \\
 & 34 & 1/2 & \pm 1/2 & 12108 & 12101 & 7 & \\
 & 35 & 1/2 & \pm 1/2 & 12128 & 12120 & 8 & \\
 & 36 & 3/2 & \pm 9/2 & 12173 & 12185 & -12 & \sigma = 8.3 \\
\textsuperspace{\textsuperscript{4}T}\textsubscript{9/2} & 37 & 1/2 & \pm 5/2 & 12865 & 12875 & -9 & \\
 & 38 & 3/2 & \pm 3/2 & 12936 & 12929 & 7 & \\
\textsuperspace{\textsuperscript{4}S}\textsubscript{11/2} & 39 & 1/2 & \pm 1/2 & 12975 & 12975 & 0 & \\
 & 40 & 1/2 & \pm 7/2 & 12990 & 12992 & -2 & \\
\textsuperspace{\textsuperscript{4}S}\textsubscript{9/2} & 41 & 3/2 & \pm 3/2 & 13000 & 13001 & -1 & \\
\textsuperspace{\textsuperscript{4}T}\textsubscript{9/2} & 42 & 1/2 & \pm 7/2 & 13031 & 13031 & 0 & \sigma = 4.8 \\
\textsuperspace{\textsuperscript{4}T}\textsubscript{11/2} & 43 & 1/2 & \pm 1/2 & 13945 & & & \\
 & 44 & 3/2 & \pm 9/2 & 13957 & & & \\
 & 45 & 3/2 & \pm 3/2 & 14045 & & & \\
 & 46 & 1/2 & \pm 5/2 & 14084 & & & \\
 & 47 & 1/2 & \pm 7/2 & 14131 & & & \\
\hline
\end{tabular}
\end{table}

\footnote{The largest \textit{M}\textsubscript{l} component to the Stark level wave function.}
\footnote{The rms deviation for each multiplet in cm\textsuperscript{-1}. The overall standard deviation is 10.1 cm\textsuperscript{-1}.}
Table 1(b). Crystal-field splitting for energy levels of Nd\(^{3+}\):AlN (part 2)

<table>
<thead>
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<th>(2J + 1 \Gamma )</th>
<th>Doublet Level</th>
<th>Irrep (( \Gamma ))</th>
<th>( M_I )</th>
<th>( E_{\text{exp}} ) (cm(^{-1}))</th>
<th>( E_{\text{calc}} ) (cm(^{-1}))</th>
<th>( \Delta E ) (cm(^{-1}))</th>
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</table>

\(^a\)The largest \(M_I\) component to the Stark level wave function.
\(^b\)The rms deviation of the fit to each multiplet is in cm\(^{-1}\). The overall standard deviation is 10.1 cm\(^{-1}\).

\[
H_A = E_{\text{exp}} + \sum_k F^k f_k + \alpha L(L+1) + \beta G(G_z) + \gamma G(R_y) + \sum_j T^j t_j + \sigma_m A_m + \sum_k P^k p_k + \sum M^j m_j
\]

and non-spherically-symmetric contributions from the one electron crystal field,

\[
H_{\text{cf}} = \sum_{k,q} B_{k,q}^{(1)} C_{k,q}^{(1)}
\]

In \( C_{3v} \) symmetry there are six independent \( B_{k,q}^{(1)} \) crystal-field parameters: \( B_0^0 \), \( B_1^0 \), \( B_2^0 \), \( B_0^1 \), \( B_1^1 \), and \( B_2^1 \). The experimental Stark levels were modeled through use of a Monte Carlo method in which the six parameters were given random starting values and optimized using standard least-squares fitting between calculated and experimental levels. The best overall agreement gave a fitting standard deviation of 10.1 cm\(^{-1}\). This value can be compared to the standard deviation of 9.7 cm\(^{-1}\) obtained with the 14-parameter \( C_{1h} \) crystal-field. We then tested the validity of these fits by comparing the Zeeman splitting calculated for a 6 T magnetic field with the experimental splittings. The energy level calculations determined from the \( C_{3v} \) symmetry fit yielded results in closer agreement to experiment than those of the \( C_{1h} \) symmetry fit. This indicates that the modest fitting improvement in the energy level calculations given by the \( C_{1h} \) symmetry calculations may be an artifact of the increase in the number of fitted parameters, rather than having physical significance. For this reason, we report energy levels (Tables 1(a) and 1(b)) and Zeeman splittings (Table 3) calculated assuming \( C_{3v} \) symmetry, along with the experimental values.

Tables 1(a) and 1(b) present energy levels and group theoretical irreducible representations (irreps), \( \Gamma_{1/2} \) and \( \Gamma_{3/2} \), calculated for \( C_{3v} \) symmetry, along with the experimental energy levels for the main “a” site. The Zeeman data presented in Table 3 confirm that the calculated irreps are correctly ordered for the first four energy levels of the ground configuration, \( ^4 \text{H}(2)_{3/2} \). Final atomic and crystal-field parameters are listed in Table 2. The overall fit has a standard deviation of 10.1 cm\(^{-1}\) (rms error = 8.0 cm\(^{-1}\)). Nine of the 20 atomic parameters were allowed to vary in the fitting process, along with all six crystal-field parameters. Parameter uncertainties for these 15 parameters are given in parentheses after the parameter values. The other 11 atomic parameters were held fixed at previously determined values.

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Table 2. Calculated atomic and crystal-field parameters (in cm$^{-1}$) for Nd$^{3+}$:AlN and Nd$^{3+}$:GaN $^{[16]}$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Nd$^{3+}$:AlN (cm$^{-1}$)</th>
<th>Nd$^{3+}$:GaN (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{0}$</td>
<td>20951 (170)</td>
<td>21766 (57)</td>
</tr>
<tr>
<td>$E_{2}$</td>
<td>49242 (1630)</td>
<td>56414 (503)</td>
</tr>
<tr>
<td>$E_{4}$</td>
<td>55222 (338)</td>
<td>52840 (216)</td>
</tr>
<tr>
<td>$E_{6}$</td>
<td>19666 (755)</td>
<td>25322 (399)</td>
</tr>
<tr>
<td>$a$</td>
<td>22.8</td>
<td>22.8</td>
</tr>
<tr>
<td>$\beta$</td>
<td>$-896$ (12)</td>
<td>$-856$ (15)</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>1695</td>
<td>1695</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>669 (16)</td>
<td>753 (9)</td>
</tr>
<tr>
<td>$T_{2}$</td>
<td>2197 (244)</td>
<td>1578 (83)</td>
</tr>
<tr>
<td>$T_{3}$</td>
<td>23 (3)</td>
<td>24 (3)</td>
</tr>
<tr>
<td>$T_{4}$</td>
<td>37</td>
<td>37</td>
</tr>
<tr>
<td>$T_{5}$</td>
<td>$-244$</td>
<td>$-244$</td>
</tr>
<tr>
<td>$T_{6}$</td>
<td>399</td>
<td>399</td>
</tr>
<tr>
<td>$T_{8}$</td>
<td>301</td>
<td>301</td>
</tr>
<tr>
<td>$M_{0}$</td>
<td>0.95</td>
<td>0.95 (0.77)</td>
</tr>
<tr>
<td>$M_{1}$</td>
<td>0.56 $M_{0}$</td>
<td>0.56 $M_{0}$</td>
</tr>
<tr>
<td>$M_{2}$</td>
<td>0.38 $M_{0}$</td>
<td>0.38 $M_{0}$</td>
</tr>
<tr>
<td>$P_{0}$</td>
<td>3945 (327)</td>
<td>2299 (128)</td>
</tr>
<tr>
<td>$P_{1}$</td>
<td>0.75 $P_{2}$</td>
<td>0.75 $P_{2}$</td>
</tr>
<tr>
<td>$P_{2}$</td>
<td>0.50 $P_{2}$</td>
<td>0.50 $P_{2}$</td>
</tr>
<tr>
<td>$B_{a}$</td>
<td>109 (51)</td>
<td>242 (40)</td>
</tr>
<tr>
<td>$B_{b}$</td>
<td>1811 (61)</td>
<td>617 (53)</td>
</tr>
<tr>
<td>$B_{e}$</td>
<td>$\pm 1113$ (65)</td>
<td>$\pm 1516$ (30)</td>
</tr>
<tr>
<td>$B_{i}$</td>
<td>136 (61)</td>
<td>$-434$ (30)</td>
</tr>
<tr>
<td>$B_{i}$</td>
<td>$\pm 414$ (42)</td>
<td>$\pm 366$ (25)</td>
</tr>
<tr>
<td>$B_{i}$</td>
<td>$-458$ (44)</td>
<td>$-69$ (44)</td>
</tr>
</tbody>
</table>

$^{a}$Values in parenthesis indicate uncertainties (in cm$^{-1}$) in fitted parameters; other parameters were held fixed.

Table 3 presents experimental and calculated Zeeman splitting for the Stark levels of the $^{4}I_{9/2}$, $^{4}I_{3/2}$, $^{4}G_{5/2}$ and $^{4}G_{7/2}$ multiplet manifolds. In addition to the experimental and calculated Zeeman splittings for a 6 T magnetic field directed parallel and perpendicular to the crystallographic $c$-axis, 6 T Zeeman splittings for Nd:GaN $^{[16]}$ are given for comparison. We find the g-factor of the ground state somewhat smaller for Nd$^{3+}$ in the main “a” site in AlN relative to GaN. The g-factor for the minority “b” site for Nd$^{3+}$ in AlN is larger, however we lack sufficient optical data on the “b” site to further refine the details of the Zeeman splitting of this site. The inhomogeneous broadening of the transitions in the Zeeman spectra further reduces our ability to determine small g-factors associated with the Zeeman data of both the “a” and “b” sites. However, a sufficient number of Stark levels are reported in Tables 1(a) and 1(b) for modeling of the crystal field and Zeeman splittings, which yield reasonable agreement between the calculated and experimental g-factors, as shown in Table 3.
Table 3. Splitting of 4f (main site) crystal-field energy levels in a 6 T magnetic field (in cm$^{-1}$), and resultant g-values for energy levels of Nd$^{3+}$:AlN

| $^{5}d_{J}$ | Energy Level $(cm^{-1})$ | Doublet Level | Irep | Magnetic field || s-axis | g_{cusp} | Magnetic field || c-axis | g_{cusp} |
|-----------|-----------------------|---------------|------|----------------|---------|-----------|----------------|---------|-----------|---------|
| $^{4}I_{9/2}$ | 0 | 1 | 3/2 | 11.3 | 10.5 | 13.4 | 4.1 $\pm$ 0.4 | 0.3 | 0.3 | 0.0 | 0.11 $\pm$ 0.2 |
| | 150 | 2 | 1/2 | 0.4 | 0 | 2.8 | $<0.5$ | 8.1 | 8.9 | 9.8 | 3.5 $\pm$ 0.3 |
| | 226 | 3 | 1/2 | 7.0 | 0 | 4.2 | $<0.5$ | 0 | $>2$ | 6.8 | $>1$ |
| | 298 | 4 | 3/2 | 11.5 | $>2$ | 10.0 | $>1$ | 0 | 0 | 0.0 | — |
| | 405 | 5 | 1/2 | 0.2$^{b}$ | — | 7.4 | — | — | 6.8 | — |
| $^{4}F_{3/2}$ | 10935 | 27 | 1/2 | 1.3 | — | 2.2 | — | 0.7 | — | 1.7 | — |
| | 10976 | 28 | 3/2 | 2.0 | — | 3.3 | — | 0 | — | 0.0 | — |
| $^{4}G_{9/2}$ | 16038 | 54 | 3/2 | 2.3$^{b}$ | — | 2.5 | — | 0$^{b}$ | — | 0.0 | — |
| | 16127 | 55 | 1/2 | — | — | 4.2 | — | — | — | 0.6 | — |
| | 16330 | 56 | 1/2 | 2.7 | — | 4.1 | — | 2.3 | — | 0.1 | — |
| $^{4}G_{7/2}$ | 16559 | 57 | 1/2 | — | — | 14.6 | — | — | — | 1.0 | — |
| | 16593 | 58 | 3/2 | — | — | 8.1 | — | — | — | 0.2 | — |
| | 16627 | 59 | 1/2 | 0 | — | 9.4 | — | 2.9 | — | 2.0 | — |
| | 16648 | 60 | 1/2 | — | — | 4.0 | — | 1.1 | — | 5.4 | — |

$^{a}$Experimental splittings for GaN from [16].

$^{b}$Levels (4,5) and (54,55) reversed for GaN, compared to AlN.

5. Summary and conclusions

The crystal-field splitting of the energy levels of Nd$^{3+}$ in AlN has been modeled assuming that the Nd$^{3+}$ ions occupy vacant Al$^{3+}$ sites in the “a” or main site in the lattice having an approximate C$_{3v}$ symmetry. Symmetries lower than C$_{3v}$, such as C$_{4h}$, were also examined to determine if size distortion involved a lower site symmetry. With the exception of an improved fit for the splitting of the $^{4}F_{3/2}$ manifold when assuming C$_{4h}$ symmetry, no significant improvement was obtained for the remaining nine multiplet manifolds investigated, including $^{4}I_{9/2}$. However, the experimental Zeeman data agree better with the calculated Zeeman splitting assuming C$_{3v}$ symmetry than it does when compared to the calculated Zeeman splitting based on C$_{4h}$ symmetry. We conclude that the best description of the crystal-field splitting and the Zeeman splitting are approximated by C$_{3v}$ symmetry. Comparisons were also made with the Zeeman data reported for Nd$^{3+}$ in GaN, which we reported earlier using a C$_{3v}$ model for the crystal-field and Zeeman splitting as well. The ordering of Stark levels are similar with the exception that levels (4,5) and (54,55) are reversed. The g-factor of Nd$^{3+}$ in the ground state of the main site is smaller in AlN than in GaN, but for the minority “b” site the g-factor is larger in AlN. Both Nd$^{3+}$-doped nitrides in the hexagonal phase examined exhibited spectra associated with minority sites. For roughly the same concentration of Nd, the minority site spectrum in AlN is stronger than observed in GaN. Given the size difference between Nd:Al, when compared to Nd:Ga, this is not surprising, given that vacancies found in both systems give rise to complexes with the dopant.

Acknowledgments

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