Crystal-field analysis and Zeeman splittings of energy levels of Nd$^{3+}$ ($4f^3$) in GaN

John B. Gruber,1 Gary W. Burdick,2 Nathaniel T. Woodward,3 Volkmar Dierolf,3 Sreerenjini Chandra,1 and Dhiraj K. Sardar1,a)

1Department of Physics and Astronomy, The University of Texas at San Antonio, San Antonio, Texas 78249–0697, USA
2Department of Physics, Andrews University, Berrien Springs, Michigan 49104–0380, USA
3Department of Physics, Lehigh University, 16 Memorial Drive East, Bethlehem, Pennsylvania 18105, USA

(Rceived 15 February 2011; accepted 9 July 2011; published online 25 August 2011)

The crystal-field splitting and Zeeman splitting of energy levels of Nd$^{3+}$ ($4f^3$) doped into semiconducting GaN (3.2 eV) grown in the hexagonal (hunite) phase by plasma-assisted molecular beam epitaxy have been modeled using a parameterized Hamiltonian defined to operate within the complete $4f^3$ electronic configuration of Nd$^{3+}$ substituted for Ga$^{3+}$ in the lattice. Zeeman splittings were obtained by applying magnetic fields up to 6.6 T with the fields parallel and perpendicular to the crystallographic c-axis. The experimental energy (Stark) levels were obtained from a recent spectroscopic study on the same samples, where the combined excitation emission spectroscopy (CEES) identified the majority of Nd$^{3+}$ ions as replacing Ga$^{3+}$ in sites of C$_{3v}$ symmetry. The manifolds of Nd$^{3+}$ ($4f^3$)$^{2S+1}L_J$ modeled for the crystal-field splitting include the ground state, $^4I_{9/2}$, and excited states $^4I_{11/2}$, $^4I_{13/2}$, $^4F_{3/2}$, $^4F_{5/2}$, $^2H_{9/2}$, $^4F_{7/2}$, $^2S_{3/2}$, $^2G_{5/2}$, and $^2G_{7/2}$. The energies of 41 experimental Stark levels from these manifolds were modeled through the use of a Monte Carlo method in which independent crystal-field parameters (CFP) were given random starting values and optimized using standard least-squares fitting between calculated and experimental Stark levels. Irreducible representations (irreps) and crystal field quantum numbers ($\mu$) were assigned to the energy levels states of the $^4I_{9/2}$ and $^4F_{3/2}$ multiplet manifolds based on an analysis of the Zeeman data. This allows determination of which of the competing local minima should be considered to be the physically significant minimum. Using standard least-squares fitting between calculated and experimental Stark levels for Nd$^{3+}$ in C$_{3v}$ symmetry, we obtain a final standard deviation of 7.01 cm$^{-1}$ (rms = 5.48 cm$^{-1}$). © 2011 American Institute of Physics.

I. INTRODUCTION

Wide bandgap semiconductors such as GaN (3.2 eV) and AlN (6.1 eV) doped with rare-earth ions (RE$^{3+}$) are characterized by optical and electrical properties that make them increasingly important components in a growing market for photonic devices.1,2 Their robust mechanical properties and high thermal conductivity make them attractive components in high-power/high-temperature controller devices.2,3 Sharp fluorescence lines are observed over a wide range of emission frequencies within the bandgap due to electronic transitions within the well-shielded $4f^n$ electronic shell.4,5 Sample excitation, both above and within the bandgap, results in emission to Stark-level components of numerous multiplet manifolds ($^{2S+1}L_J$) of the RE$^{3+}$ $4f^n$ configuration.4–6 The basic science reported on these doped nitrides over the years is a leading factor in their current success in emerging technologies.7–11 Because of interest in the nitrides as potential laser hosts and light-emitting diodes, we have analyzed previously the spectra and the crystal-field splitting of several RE$^{3+}$ ions implanted in GaN and AlN thin films.12–14 A detailed study of the spectra and the crystal-field splitting of Yb$^{3+}$ in AlN has been reported more recently by Koubaa et al.15

Recently, Readinger et al.16 reported the fabrication of in situ doping of GaN with Nd by plasma-assisted molecular beam epitaxy (PA-MBE). Metcalfe et al.17 followed this work with an optical characterization of the observed Nd$^{3+}$ emission spectra. Using site-selective excitation methods, Metcalfe et al.17 identified several Nd$^{3+}$ sites in the doped samples, including a majority site, which they suggested contained Nd$^{3+}$ ions that had replaced Ga$^{3+}$ ions in cation sites having C$_{3v}$ symmetry in undoped GaN. The set of experimental crystal-field split energy (Stark) levels identified as the “main” site in Ref. 17, were used in the present study to model the crystal-field splitting of the $^{2S+1}L_J$ multiplet manifolds of Nd$^{3+}$, which include the ground-state manifold, $^4I_{9/2}$, and the excited manifolds $^4I_{11/2}$, $^4I_{13/2}$, $^4F_{3/2}$, $^4F_{5/2}$, $^2H_{9/2}$, $^4F_{7/2}$, $^2S_{3/2}$, $^2G_{5/2}$, and $^2G_{7/2}$.

The size difference between Nd$^{3+}$ and Ga$^{3+}$ and the energetics of substitution may affect the local environment, resulting in a lower site symmetry for Nd$^{3+}$ in GaN. In order to investigate the effects of distortions from a true C$_{3v}$ site symmetry for the substituted Nd$^{3+}$ ions, 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$_{1d}$ (assuming the mirror plane symmetry remains, but the threefold rotation axis symmetry is broken). Although the number

---

a)Author to whom correspondence should be addressed. Electronic mail: dhiraj.sardar@utsa.edu.
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 improvement in the energy level fitting standard deviation is achieved with inclusion of these additional parameters. Additionally, no significant changes in calculated Zeeman g-values were observed between corresponding fits to each of the three symmetries. For this reason, calculations reported below assume that the Nd^{3+} ion occupies sites of approximate C_3v symmetry.

II. ANALYSIS OF THE ZEEMAN SPLITTING

Following up on the interpretation of the experimental energy (Stark) levels obtained from the analysis of the combined excitation emission spectroscopy (CEES) reported in Ref. 17, we have extended those measurements to the determination of Zeeman splittings and g-factors by applying magnetic fields of up to 6.6 T. Fields have been applied both in the in-plane (perpendicular to the c-axis) and out-of-plane (parallel to the c-axis) directions. Such studies have proven to be very valuable in assigning the irreducible representations (irreps) and the crystal field quantum numbers (\( \ell \)) to the respective Stark levels. Either designation can be used to describe the symmetry characteristics of the wavefunction associated with each Stark level. In C_3v symmetry, the Stark levels will be split for the field along the c-axis, while only \( \Gamma_{1/2} \) levels will split for the perpendicular field. We obtained data by first exciting the \( ^4G_{5/2} \) and \( ^2G_{7/2} \) states. The emission was detected for the transitions from \( ^4F_{3/2} \) to the \( ^4I_{9/2} \) ground-state manifold. As a result of the number of levels involved, each peak in the zero-field excitation-emission map of Ref. 17 can be split into as many as \( 2^4 - 1 = 16 \) peaks, reflecting the comprehensive data set, which is obtained by CEES, enabling us to assign the splitting to the respective Stark levels.

Figure 1 shows the results for in and out-of-plane magnetic fields (0–6 T) for a selected excerpt of data. We see several peaks that have been split in both emission and excitation, allowing us to identify several g-factors in excited and ground states of Nd^{3+}. By comparing the behavior of the excitation and emission transitions labeled A, B, C, D, E, and F, it is apparent that respective Zeeman splittings are clearly different for the fields applied in the two orthogonal directions. While C, D, and E split for parallel fields, the most pronounced splittings occur for A, B, and F for perpendicular fields. In order to illustrate the strategy for how the various splittings are correlated with g-factors of particular levels, we focus first on the results for out-of-plane fields and the emission to the two closely spaced lowest ground Stark levels.

In Fig. 2 we show the emission obtained under the application of a magnetic field of 6 T. In determining g-factors, we take advantage of the fact that the several emission peaks share a common final level (see inset in Fig. 2). For instance, the peak labeled B is the emission due to the upper thermally excited Stark level of \( ^4F_{3/2} \) that is shifted by about 4 meV (34 cm\(^{-1}\)) to higher energy from peak A, which corresponds to the lower energy Stark level in the \( ^4F_{3/2} \) manifold. The same is true for peaks C and D, which correspond to transitions to the lowest ground-state Stark level. For fields parallel to the c-axis, the emission of the latter pair is clearly split, while A and B are not, thus indicating that the ground state and not the excited \( ^4F_{3/2} \) Stark level represents the origins of the splitting of C and D. The splitting of the excited states is small, as seen by the fact that none of the emission peaks split into more than two peaks, even in fields as high as 6 T. Only for C and D do we see a small broadening of the peaks.

The splitting can be converted to effective g-factors using the expression \( \Delta E = \mu_B g_{\text{eff}} B \); where the energy splitting, the Bohr magneton, and the magnitude of the magnetic field are known. For example, the g-factor for the ground...
state is calculated from the data to be 4.03. Using this result, the broadening of the peaks can be exploited to calculate the splitting of the excited $^4I_{9/2}$ Stark levels. For that we use the methods of moments and assume an unresolved splitting of the respective zero-field Gaussian-shaped peak. Under this assumption, the splitting is determined by the change in the second moment of the spectrum. Once we have the $g$-factors of the $^4I_{9/2}$ Stark levels, we can determine the splitting for cases in which the splitting of the final state is small. In this way we can assign effective $g$-values to each Stark level in the $^4I_{9/2}$ manifold for this sample orientation beginning with the ground state Stark level: 4.03, 0.14, 2.51, 0.09, and 4.12.

The order of the energy of the Stark levels in cm$^{-1}$ in the $^4I_{9/2}$ manifold is 0, 48, 211, 245, and 323 cm$^{-1}$, as shown in Table I.

We can then repeat the procedure for magnetic fields applied in-plane by rotating the sample by 90 degrees in the sample chamber, and for consistency, we maintain the excitation along the $c$-axis of the sample. Thus, the emission and excitation spectra at zero-magnetic field are identical to the parallel magnetic field case and we can readily identify changes in the $g$-factors using the method just described, except that the two lowest ground-state Stark levels exchange their role. In this case only the A and B transitions exhibit a splitting, suggesting that the second lowest Stark level is responsible for this splitting while the other splittings are small. In this case, following the same ordering of the Stark levels for $^4I_{9/2}$ as reported earlier, the $g_{\text{eff}}$ are 0.12, 2.91, 0.0, 0.14, and 0.0 in the applied magnetic field in-plane orientation (see Table I). For Kramer’s doublet states in $C_{3v}$ symmetry, the group theoretical irreducible representations (irreps) are $\Gamma_{1/2}$ and $\Gamma_{3/2}$. They represent the group symmetry labels used to characterize the wavefunction of individual Stark levels. The individual states can be assigned crystal field quantum numbers as well. In $C_{3v}$ symmetry these designations are represented as $\mu = \pm 1/2$ and $\mu = \pm 3/2$. They are assigned to states characterized by the irreps of $\Gamma_{1/2}$ and $\Gamma_{3/2}$, respectively. Stark levels that exhibit substantial splittings in magnetic fields applied perpendicular to the $c$-axis can be assigned to a $\Gamma_{1/2}$ state, while levels with zero (or small) splittings may be assigned to a possible $\Gamma_{3/2}$ state. In principle, the irreps and the crystal-field quantum numbers ($\mu$) can be assigned to the experimental Stark levels based on an analysis of the Zeeman data.

The energy values of all experimental Stark levels reported in Ref. 17 were converted into wavenumbers (cm$^{-1}$) through the conversion factor 8.065541 cm$^{-1}$/meV. Grace Metcalfe kindly allowed us to review the original emission and excitation data obtained at the Army Adelphi Center (ARL). We determined a few changes from the published levels in Ref. 17. Two of the reported Stark levels associated with the main site, namely 1470.8 meV (11863 cm$^{-1}$) and 1498.0 meV (12082 cm$^{-1}$) appear to be transitions from level 2 in Table I to excited Stark levels at 1476.6 meV (11910 cm$^{-1}$), and 1503.8 meV (12129 cm$^{-1}$) (Levels 29 and 33 in Table I). Levels 32 and 36 were assigned by analyzing the original data to obtain excited Stark levels at 12120 cm$^{-1}$ and 12207 cm$^{-1}$, respectively; levels 41 and 42 were obtained by de-convoluting the peak

<table>
<thead>
<tr>
<th>$^{2S+1}L_J$</th>
<th>Doublet level</th>
<th>$\text{Irrep}^a (\Gamma)$</th>
<th>$M_J^b$</th>
<th>$E_{\text{exp}}$ (cm$^{-1}$)</th>
<th>$E_{\text{calc}}$ (cm$^{-1}$)</th>
<th>$\Delta E$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4I_{9/2}$</td>
<td>1</td>
<td>3/2</td>
<td>±9/2</td>
<td>0</td>
<td>1</td>
<td>−1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1/2</td>
<td>±1/2</td>
<td>48</td>
<td>39</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1/2</td>
<td>±7/2</td>
<td>211</td>
<td>213</td>
<td>−2</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1/2</td>
<td>±5/2</td>
<td>245</td>
<td>246</td>
<td>−1</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>3/2</td>
<td>±3/2</td>
<td>323</td>
<td>321</td>
<td>2</td>
</tr>
<tr>
<td>$^4I_{11/2}$</td>
<td>6</td>
<td>1/2</td>
<td>±11/2</td>
<td>1879</td>
<td>1897</td>
<td>−17</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>3/2</td>
<td>±9/2</td>
<td>1914</td>
<td>1915</td>
<td>−1</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>1/2</td>
<td>±1/2</td>
<td>1948</td>
<td>1944</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>1/2</td>
<td>±7/2</td>
<td>2054</td>
<td>2055</td>
<td>−1</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>3/2</td>
<td>±3/2</td>
<td>2075</td>
<td>2075</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>1/2</td>
<td>±5/2</td>
<td>2090</td>
<td>2088</td>
<td>2</td>
</tr>
<tr>
<td>$^4I_{13/2}$</td>
<td>12</td>
<td>1/2</td>
<td>±13/2</td>
<td>3844</td>
<td>3842</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>1/2</td>
<td>±11/2</td>
<td>3865</td>
<td>3859</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>3/2</td>
<td>±3/2</td>
<td>3898</td>
<td>3893</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>1/2</td>
<td>±1/2</td>
<td>3921</td>
<td>3934</td>
<td>−13</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>3/2</td>
<td>±9/2</td>
<td>4041</td>
<td>4044</td>
<td>−3</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>1/2</td>
<td>±5/2</td>
<td>4067</td>
<td>4067</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>1/2</td>
<td>±7/2</td>
<td>4090</td>
<td>4080</td>
<td>10</td>
</tr>
<tr>
<td>$^4I_{15/2}$</td>
<td>19</td>
<td>1/2</td>
<td>±13/2</td>
<td>5840</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>3/2</td>
<td>±15/2</td>
<td>5866</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>1/2</td>
<td>±11/2</td>
<td>5933</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>22</td>
<td>1/2</td>
<td>±1/2</td>
<td>5954</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>23</td>
<td>3/2</td>
<td>±3/2</td>
<td>6009</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>1/2</td>
<td>±5/2</td>
<td>6183</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>1/2</td>
<td>±7/2</td>
<td>6227</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>26</td>
<td>3/2</td>
<td>±9/2</td>
<td>6237</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Irreps: $C_3$, $C_3^r$, $C_3v$, $C_3$, $C_3^r$.

$^b$Crystal-field quantum numbers: $\lambda = 0, 4, 8, 12, 16, 20, 24, 28$.
Following standard practice, this model includes spherically symmetric “atomic” contributions, given by assuming the Nd$^{3+}$ to operate within the entire 4$S$ manifold. Within experimental measurement, the remainder of the Stark levels determined are in agreement with those reported in the present study are in agreement with those reported.

III. CRYSTAL-FIELD MODELING STUDIES

The crystal-field splitting of 41 experimental Stark levels were modeled using a parameterized Hamiltonian defined to operate within the entire 4$S$ electronic configuration assuming the Nd$^{3+}$ ions occupy sites of C$_{3v}$ symmetry. Following standard practice, this model includes spherically symmetric “atomic” contributions, given by

$$H_A = E_{\text{avg}} + \sum_k F^i_k + \alpha L(L + 1) + \beta G(G_2) + \gamma G(R_7)$$

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

$$H_{\text{cr}} = \sum_{kq} b^k_q C^{(k)}_{q}. $$

For ions in C$_{3v}$ symmetry, there are six independent B$^j_q$ crystal-field parameters: B$^1_0$, B$^2_0$, B$^4_0$, B$^6_0$, and B$^8_0$. 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 three local minima with the lowest standard deviations each correspond to different orderings of the irreducible representations (irreps) for the ground configuration $^4I_{9/2}$ states. The best fitting has a standard deviation of 5.21 cm$^{-1}$, and has ground configuration states ordered as \{C$^1_{1/2}$, C$^3_{1/2}$, C$^3_{3/2}$\}. The second-best fit has a standard deviation of 6.08 cm$^{-1}$, with ground configuration states \{C$^1_{3/2}$, C$^3_{1/2}$, C$^3_{3/2}$\}. The third-best fit has a standard deviation of 7.01 cm$^{-1}$, with ground configuration states \{C$^1_{1/2}$, C$^3_{1/2}$, C$^3_{3/2}$\}. However, when the Zeeman splitting of the ground configuration states are examined, it is clear that only the third-best fit can rationalize the experimental data. Thus, it is this third-best fit that is presented along with the experimental energy levels in Table I.

Table I gives a comparison between the experimental levels (column 5) and the calculated levels (column 6), assuming C$_{3v}$ symmetry, with the energy difference in column 7. The irrep identification and largest $M_f$ components for each Kramer’s doublet level are given in columns 3 and 4.

<table>
<thead>
<tr>
<th>$^{2S+1}L_J$</th>
<th>Doublet Level</th>
<th>Irrep$^a$ (Γ)</th>
<th>$E_{\text{exp}}$ (cm$^{-1}$)</th>
<th>$E_{\text{calc}}$ (cm$^{-1}$)</th>
<th>$\Delta E$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>51</td>
<td>1/2</td>
<td>±1/2</td>
<td>15298</td>
<td>15201</td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>3/2</td>
<td>±3/2</td>
<td>15301</td>
<td>15307</td>
<td></td>
</tr>
<tr>
<td>53</td>
<td>1/2</td>
<td>±1/2</td>
<td>15307</td>
<td>15307</td>
<td></td>
</tr>
<tr>
<td>$^4G_{5/2}$</td>
<td>54</td>
<td>1/2</td>
<td>±1/2</td>
<td>16032</td>
<td>16037</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>3/2</td>
<td>±3/2</td>
<td>16119</td>
<td>16110</td>
</tr>
<tr>
<td></td>
<td>56</td>
<td>1/2</td>
<td>±1/2</td>
<td>16315</td>
<td>16321</td>
</tr>
<tr>
<td></td>
<td>57</td>
<td>1/2</td>
<td>±1/2</td>
<td>16538</td>
<td>16534</td>
</tr>
<tr>
<td></td>
<td>58</td>
<td>3/2</td>
<td>±3/2</td>
<td>16543</td>
<td>16549</td>
</tr>
<tr>
<td></td>
<td>59</td>
<td>1/2</td>
<td>±1/2</td>
<td>16561</td>
<td>16559</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>1/2</td>
<td>±1/2</td>
<td>16607</td>
<td>16605</td>
</tr>
</tbody>
</table>

$^a$ Irreducible representation; crystal-quantum numbers ±1/2 and ±3/2 are assigned to states characterized by irreps Γ$_{1/2}$ and Γ$_{3/2}$, respectively.

$^b$ The largest $M_f$ component to the Stark level wave function.

$^c$ The rms deviation for each multiplet in cm$^{-1}$.

TABLE II. Splitting of crystal-field energy levels in a 6.6 T magnetic field (in cm$^{-1}$), and resultant g-values for energy levels of Nd$^{3+}$:GaN.

<table>
<thead>
<tr>
<th>$^{2S+1}L_J$</th>
<th>Magnetic field \parallel c-axis</th>
<th>Magnetic field \perp c-axis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{\text{exp}}$</td>
<td>$E_{\text{calc}}$</td>
</tr>
<tr>
<td>$^4I_{9/2}$</td>
<td>1</td>
<td>3/2</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1/2</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1/2</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1/2</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>3/2</td>
</tr>
<tr>
<td>$^4F_{3/2}$</td>
<td>27</td>
<td>1/2</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>3/2</td>
</tr>
<tr>
<td>$^4G_{5/2}$</td>
<td>54</td>
<td>1/2</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>3/2</td>
</tr>
<tr>
<td></td>
<td>56</td>
<td>1/2</td>
</tr>
<tr>
<td>$^4G_{7/2}$</td>
<td>57</td>
<td>1/2</td>
</tr>
<tr>
<td></td>
<td>58</td>
<td>3/2</td>
</tr>
<tr>
<td></td>
<td>59</td>
<td>1/2</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>1/2</td>
</tr>
</tbody>
</table>

$^a$ Irreducible representation; crystal-quantum numbers ±1/2 and ±3/2 are assigned to states characterized by irreps Γ$_{1/2}$ and Γ$_{3/2}$, respectively.
The calculated magnetic field splittings for states in the $4I_{9/2}$, respectively, as listed in column 3. Experimental and transition between $4F_{3/2}$ and $4I_{11/2}$ in GaN is shifted to lower multiplets. The energy difference for the well-known lasing shift is especially apparent between the $4I$ shown in Table IV, which compares the Nd$^{3+}$ barycenters obtained in three popular host crystals to the semiconducting film GaN. The intra-$4f^n$ transition probabilities are usually calculated in terms of the mixing of electronic states of opposite parity through the odd terms of the crystal-field Hamiltonian.\textsuperscript{4,5} In Nd$^{3+}$, these states are higher in energy than the onset of the bandgap in GaN, where intrinsic impurities and defect centers are found. Wave functions from these states may mix with the excited states of Nd$^{3+}$ and contribute to the barycenter shifts, emission line strengths, and decay lifetimes observed in the semi-conductor host that are distinctive from similar spectroscopic measurements obtained from Nd$^{3+}$ doped into insulator host materials.\textsuperscript{12–15,22} Jadwisin-zak \textit{et al.}\textsuperscript{11} have explored excitation mechanisms involving Eu$^{3+}$ in GaN that may be germane for a similar study of Nd$^{3+}$ in GaN. The energy shift of the manifolds of Nd$^{3+}$ from LaF$_3$ to LaCl$_3$ to Y$_2$O$_3$ to GaN as shown in Table IV may be described as a nephelauxetic shift associated with an increased covalent contribution to the bonds in GaN, relative to the ionic bonding in insulator host materials. The infrared shift in emission frequencies observed in other RE$^{3+}$-doped GaN and AlN as well \textsuperscript{13–15} opens up possibilities for future photonic applications for these emission frequencies, and deserves further fundamental studies of the energy transfer, including quantum cutting, in these materials.

**ACKNOWLEDGMENTS**

We wish to thank L. D. Merkle and G. D. Metcalfe, Army Research Laboratory (ARL), for helpful discussions and G. D. Metcalfe for access to the data appearing in Ref. 17. J.B.G. wishes to acknowledge the Battelle Scientific Services Program (TCN 09141) for financial support while analyzing the experimental data at ARL.

\begin{table}[h]
\centering
\caption{Calculated atomic and crystal-field parameters (in cm$^{-1}$) for Nd$^{3+}$:GaN. Values in parentheses indicate uncertainties (in cm$^{-1}$) in fitted parameters; other parameters were held fixed.}
\begin{tabular}{ll}
\hline
Parameter & Value (cm$^{-1}$) \\
\hline
$E_{\text{avg}}$ & 21766 (57) \\
$F_2$ & 56414 (503) \\
$F_4$ & 52840 (216) \\
$F_6$ & 25322 (399) \\
$\alpha$ & 22.8 \\
$\beta$ & $-856$ (15) \\
$\gamma$ & 1695 \\
$\xi$ & 753 (9) \\
$T_2$ & 1578 (83) \\
$T_3$ & 24 (3) \\
$T_4$ & 37 \\
$T_6$ & $-241$ \\
$T_7$ & 399 \\
$T_8$ & 301 \\
$M_0$ & 0.95 (0.77) \\
$M_2$ & 0.56 $M_0$ \\
$M_4$ & 0.38 $M_0$ \\
$P_2$ & 2299 (128) \\
$P_4$ & 0.75 $P_2$ \\
$P_6$ & 0.50 $P_2$ \\
$B_{10}^0$ & 242 (40) \\
$B_{10}^0$ & 617 (53) \\
$B_{10}^0$ & $\pm 1516$ (30) \\
$B_{10}^0$ & $-434$ (30) \\
$B_{10}^0$ & $\pm 366$ (25) \\
$B_{10}^0$ & $-69$ (44) \\
\hline
\end{tabular}
\end{table}

\begin{table}[h]
\centering
\caption{Experimental barycenters (in cm$^{-1}$) for Nd$^{3+}$ ($4f^n$). Data obtained from Ref. 23.}
\begin{tabular}{ccccccc}
\hline
$25^{\text{th}}$ & $I_J$ & LaF$_3$ & LaCl$_3$ & Y$_2$O$_3$ & GaN & $\Delta E_1$ & $\Delta E_2$
\hline
$4I_{15/2}$ & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
$4I_{11/2}$ & 1902 & 1882 & 1880 & 1828 & 74 & 52 & 0 \\
$4I_{13/2}$ & 3892 & 3865 & 3846 & 3796 & 96 & 50 & 0 \\
$4I_{11/2}$ & 5970 & 5932 & 5885 & & & & \\
$4F_{5/2}$ & 11418 & 11293 & 11029 & 10769 & 649 & 260 & 0 \\
$4F_{5/2}$ & 12343 & 12330 & 12008 & 11793 & 641 & 215 & 0 \\
$2H_{11/2}$ & 12568 & 12454 & 12291 & 12000 & 568 & 291 & 0 \\
$2G_{7/2}$ & 13418 & 13294 & 13069 & 12764 & 654 & 305 & 0 \\
$4S_{3/2}$ & 13518 & 13386 & 13141 & 12826 & 692 & 315 & 0 \\
$4F_{7/2}$ & 14699 & 14577 & 14307 & & & & \\
$2H_{11/2}$ & 15872 & 15799 & 15561 & & & & \\
$4G_{7/2}$ & 17133 & 17017 & 16476 & 15990 & 1143 & 486 & 0 \\
$2G_{7/2}$ & 17357 & 17251 & 16890 & 16397 & 960 & 493 & 0 \\
$4G_{7/2}$ & 19045 & 18886 & 18365 & & & & \\
$4G_{9/2}$ & 19450 & 19319 & 18951 & & & & \\
$2P_{1/2}$ & 23278 & 23069 & 22635 & & & & \\
\hline
\end{tabular}
\end{table}


