Inter-Stark Energy Levels and Effects of Temperature on Sharp Emission Lines of Nd$^{3+}$ in LiYF$_4$

D. K. Sardar and R. M. Yow

Division of Earth and Physical Sciences, The University of Texas at San Antonio, San Antonio, Texas 78249, USA

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The inter-Stark components of the $^4I_{9/2}$ and $^4I_{11/2}$ manifolds have been characterized using the room-temperature fluorescence spectra for the $^4F_{3/2} \rightarrow ^4I_{9/2}$ and $^4F_{3/2} \rightarrow ^4I_{11/2}$ transitions of Nd$^{3+}$ in LiYF$_4$ laser crystal. The thermal effects on the linewidths, positions, and line shifts of the inter-Stark transitions of the 908 nm ($R_1 \rightarrow X_5$) and 1052.4 nm ($R_1 \rightarrow Y_2$) lines within the respective inter-manifold transitions of $^4F_{3/2} \rightarrow ^4I_{9/2}$ and $^4F_{3/2} \rightarrow ^4I_{11/2}$ have been also investigated. The linewidths of these transitions are found to increase with increasing temperature. The 908 nm line is found to shift toward the shorter wavelength, while the 1052.4 nm line has shifted toward the longer wavelength. The experimental results of the temperature-dependent widths and shifts of these sharp spectral lines are explained using the phonon–ion interaction theory which assumes the Debye model for phonons in crystalline solids.

1. Introduction

A number of rare earth ions in scheelite structured lithium yttrium fluoride, LiYF$_4$ (YLF), have been studied extensively by several authors in the past [1 to 5]. The Nd$^{3+}$:YLF has proven to be a promising candidate as an efficient laser system because of its superior thermal and optical properties [1]. For example, the large thermal conductivity of Nd$^{3+}$:YLF helps to extract the unwanted heat from the system during the optical pumping and its large natural birefringence eliminates the thermal depolarization problems that are present in such common hosts as YAG and glass [6, 7]. According to Murraay, the weak thermal lensing in Nd$^{3+}$:YLF, coupled with its natural birefringence, makes this material a better candidate than Nd$^{3+}$:YAG for high brightness as well as high average power [1]. An excellent spectroscopic analysis of Nd$^{3+}$:YLF by Ryan and Beach [4] has demonstrated that there is a negligible difference between the radiative lifetime predicted by the Judd-Ofelt theory and the measured fluorescence lifetimes of the metastable $^4F_{3/2}$ level, thereby suggesting that this material has a high quantum efficiency which is defined as the ratio of the measured and radiative lifetimes. They have also shown that the orientation emission cross-section of the $R_1 \rightarrow Y_2$ transition has a significantly large value which is of significant interest to laser design.

In this paper, a detailed characterization of energy levels of Nd$^{3+}$ ions in YLF for the $^4F_{3/2} \rightarrow ^4I_{9/2}$ and $^4F_{3/2} \rightarrow ^4I_{11/2}$ transitions has been performed using the well-resolved, room-temperature fluorescence spectra. For laser action, the thermal broadening and shift of the laser line have a significant meaning since these are closely related to the light amplification gain, output frequency stability, and thermal tunability of the laser. However, to the best of our knowledge, there have been no studies on the ther-
mal effects on the line shift and line broadening of Nd$^{3+}$ in YLF. Owing to the potential of Nd$^{3+}$:YLF as a laser material, the temperature dependences of widths, positions and shifts of the 908 and 1052.4 nm lines for the corresponding inter-Stark transitions of $R_1 \rightarrow X_5$ and $R_1 \rightarrow Y_5$ within the $^4F_{3/2} \rightarrow ^4I_{9/2}$ and $^4F_{3/2} \rightarrow ^4I_{11/2}$ intermanifold transitions, respectively, of Nd$^{3+}$ ions in this host have also been investigated. The measured temperature dependences of widths, positions and shifts of these spectral lines have been compared with the existing theory of phonon–ion interaction based on the Debye model for phonons in the host lattice that leads to the phonon-relaxation processes.

2. Experimental Details

The samples used in this study were single crystals of Nd$^{3+}$:YLF obtained from Opto-vac. The samples were doped with 1 wt% of Nd$^{3+}$ in the melt. The optical quality of the material was found to be good. The scheelite structured LiYF$_4$ crystals doped with Nd$^{3+}$ ions were grown from the melt in an inert atmosphere by the Czochralski method. The YLF is isomorphous with CaWO$_4$, both having similar lattice dimensions. During the growth of Nd$^{3+}$:YLF crystals, the substitution of Y$^{3+}$ by Nd$^{3+}$ is accomplished easily because the dimensional, chemical, and physical properties of the two ions are quite similar. The sample used for spectroscopic measurements was optically polished and the thickness of the sample was measured as 2.39 mm.

The temperature-dependent emission spectra were measured on the Nd$^{3+}$:YLF sample at ten different temperatures ranging from 10 to 300 K, by exciting the sample with the 514.5 nm line of an argon ion laser, model 2005 from Spectra Physics. The spectral bandwidth, full-width at half-maximum (FWHM), of the laser was 0.12 nm and the maximum laser power used in these measurements was kept at 4 W. The laser beam with a Gaussian profile had a $1/e^2$ radius of 0.63 mm and the beam divergence was 0.69 mrad. The fluorescence from the sample was collected at right angle with respect to the direction of the excitation laser beam and focused with a pair of lenses onto the entrance slit of a Spex monochromator model 340E which is equipped with a 600 grooves/mm grating blazed at 1.0 $\mu$m. The signal was detected by a liquid nitrogen-cooled Ge detector attached to the exit slit of the monochromator and processed by a Spex model DS 1000 Datascan equipped with a RS-232 interface card. The spectral resolution was better than 0.2 nm in all measurements. A personal computer was employed to control the monochromator and to acquire and analyze the data.

For the temperature-dependent measurements, the Nd$^{3+}$:YLF sample was mounted at the cold finger of a CTI model 22, a closed-cycle helium cryogenic refrigerator, capable of controlling temperature from about 10 to 300 K. The temperatures were controlled by a Lake Shore model 320 temperature controller and measured by a silicon diode sensor attached to the base of the sample holder.

3. Results and Data Analysis

The room temperature emission spectra for the $^4F_{3/2} \rightarrow ^4I_{9/2}$ and $^4F_{3/2} \rightarrow ^4I_{11/2}$ transitions of Nd$^{3+}$ in YLF are displayed in Figs. 1 and 2, respectively. A total of ten emission bands is clearly observed in Fig. 1 and a total of 12 emission bands is identified in Fig. 2. The relatively well-resolved inter-Stark transition within the $^4F_{3/2} \rightarrow ^4I_{9/2}$ transition has been identified as $R_1 \rightarrow X_5$ at 908 nm in Fig. 1. One of the most intense inter-
Stark transitions within the $^4F_{3/2} \rightarrow ^4I_{11/2}$ manifold transition has been identified as $R_1 \rightarrow Y_2$ at 1052.4 nm in Fig. 2. The intensities of the 908 and 1052.4 nm lines are about two to five times higher than most of the lines in the respective $^4F_{3/2} \rightarrow ^4I_{9/2}$ and $^4F_{3/2} \rightarrow ^4I_{11/2}$ manifold transitions.
3.1 Inter-Stark energy levels

The detailed characterization of the Stark energy levels of the $^4F_{3/2}$, $^4I_{9/2}$, and $^4I_{11/2}$ multiplet manifolds has been determined from the well-resolved, room-temperature emission spectra for the $^4F_{3/2} \rightarrow ^4I_{9/2}$ and $^4F_{3/2} \rightarrow ^4I_{11/2}$ transitions of Nd$^{3+}$ in the YLF host. The energy level diagrams for the Stark components for the $^4F_{3/2} \rightarrow ^4I_{9/2}$ and $^4F_{3/2} \rightarrow ^4I_{11/2}$ transitions are presented in Figs. 3 and 4, respectively. The proper ordering of the individual Stark components has been obtained using a computer model [8]. Due to their sharpness and intensity, the 908 nm line corresponding to the $R_1 \rightarrow X_5$ transition designated as 10 in Fig. 3 and the 1052.4 nm line corresponding to the $R_1 \rightarrow Y_2$ transition designated as 5 in Fig. 4 have been chosen to perform the measurements of linewidths, line shapes, and line shifts as functions of temperature.

According to Sengupta and Artman [9] the inter-Stark transition $R_2 \rightarrow X_4$ is not shown because of its weakness. This transition identified as number 7 in Fig. 1 is clearly the weakest of all ten emission bands. Wortman [10] has reported that the $^4I_{9/2}$ manifold inter-Stark splitting ranges from 0 to 529 cm$^{-1}$. This agrees well with the result of our investigation which shows that the $^4I_{9/2}$ manifold splitting ranges from 0 to 528 cm$^{-1}$. In addition, Wortman shows that the $^4I_{11/2}$ manifold inter-Stark splitting spans from 1998 to 2264 cm$^{-1}$. Our finding, however, shows that this manifold splitting ranges from 1992 to 2329 cm$^{-1}$. Wortman includes two pairs of peaks closely positioned around 1053 and 1047 nm. Our research, however, shows only one peak at each of these wavelengths and two additional peaks at 1079 and 1086 nm. Although these latter transitions.

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Fig. 3. Energy level diagram of Nd$^{3+}$ in YLF for the inter-Stark transitions between the $^4F_{3/2}$ and $^4I_{9/2}$ manifolds at 300 K.
two peaks are very weak, they become noticeable when that region of emission spectrum is blown up. More importantly, these two peaks fit well with the computer model used in this study.

### 3.2 Debye temperature

The fluorescence lines for the $R_1 \rightarrow X_5$ (908 nm) and $R_1 \rightarrow Y_2$ (1052.4 nm) transitions of Nd$^{3+}$ in YLF at 10 and 300 K are shown in Fig. 5; the solid lines represent the fluorescence lines at 300 K and the dotted lines indicate the fluorescence lines at 10 K. The intensities of these transitions are normalized to an arbitrary unit of ten. The temperature dependences of width, position, and shift of the sharp fluorescence lines are clearly observed in Fig. 5.

The shapes of the spectral lines for the $R_1 \rightarrow X_5$ and $R_1 \rightarrow Y_2$ transitions were found to be Lorentzian over the temperature range of 10 to 300 K. The average linewidth (FWHM), $\Delta \nu$ (cm$^{-1}$), due to the $R_1 \rightarrow X_5$ (908 nm) transition increased from 29.8 cm$^{-1}$ at 10 K to 38.3 cm$^{-1}$ at 300 K. The average linewidth $\Delta \nu$ (cm$^{-1}$) for the $R_1 \rightarrow Y_2$ (1052.4 nm) transition increased from 9.8 cm$^{-1}$ at 10 K to 18.3 cm$^{-1}$ at 300 K. The temperature dependences of linewidths of the $R_1 \rightarrow X_5$ and $R_1 \rightarrow Y_2$ transitions are shown in Figs. 6 and 7, respectively. All measurements were repeated three times and the error bars for the data of these transitions are shown in Figs. 6 and 7.
The thermal effects on the sharp spectral lines of the Nd\textsuperscript{3+} ions in various crystal hosts have been demonstrated by several researchers [11 to 13]. According to the existing theory [12 to 18] the linewidth of the inter-Stark transitions arises from 1. the crystal strain inhomogeneity, 2. direct one-phonon processes, 3. multiphonon processes, and

![Fluorescence spectrum of Nd\textsuperscript{3+} in YLF for the R\textsubscript{1} → X\textsubscript{5} and R\textsubscript{1} → Y\textsubscript{2} transitions at 10 K (dotted lines) and 300 K (solid lines)](image)

**Fig. 5.** Fluorescence spectrum of Nd\textsuperscript{3+} in YLF for the R\textsubscript{1} → X\textsubscript{5} and R\textsubscript{1} → Y\textsubscript{2} transitions at 10 K (dotted lines) and 300 K (solid lines)

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![Linewidth of the R\textsubscript{1} → X\textsubscript{5} transition of Nd\textsuperscript{3+} in YLF as a function of temperature. The circles represent the experimental data and the solid curve is the theoretical line (see text for explanation)](image)

**Fig. 6.** The linewidth of the R\textsubscript{1} → X\textsubscript{5} transition of Nd\textsuperscript{3+} in YLF as a function of temperature. The circles represent the experimental data and the solid curve is the theoretical line (see text for explanation)
4. Raman phonon scattering processes. At the lowest temperature, the measurable line-width of a radiative transition is in general accounted for the microscopic strains of the host crystal, which is inhomogeneous due to their random nature and therefore gives rise to a Gaussian line shape. As the crystal temperature increased, the fluorescence linewidths of the Nd$^{3+}$ ions increase invariably [15]. In this paper, we will consider only the temperature-dependent line broadening mechanism which arises from the interaction between the impurity ions and the crystalline host lattice vibrations. Therefore, the width (in cm$^{-1}$) of the $i$-th energy level is given by

$$\Delta \nu_i = \Delta \nu_i^{\text{strain}} + \Delta \nu_i^{D} + \Delta \nu_i^{M} + \Delta \nu_i^{R}.$$  

The first term, $\Delta \nu_i^{\text{strain}}$, is the width due to the crystal strains. The second term, $\Delta \nu_i^{D}$, is the width due to direct or one-phonon processes between the $i$-th energy level and other nearby levels ($j$), and consists of a temperature independent part, $\sum_{j<i} \beta_{ij}$, which is due to the spontaneous one-phonon emission, and a temperature-dependent part, $\Delta\nu_i^{D}(T)$. Since the energy separation among the Stark levels is of the order of 10 to 10$^2$ cm$^{-1}$ in rare earths, the temperature-independent one-phonon emission could produce observable line broadening. The third term, $\Delta \nu_i^{M}$, in Eq. (1) is the contribution to the width from multiphonon emission processes, which are temperature independent and negligible in the temperature range of interest [17]. The last term $\Delta \nu_i^{R}$ represents the width of the Raman multiphonon process associated with phonon scattering by impurity ions. The Raman scattering process consists of the absorption of one phonon and the emission of another phonon without changing the electronic state of the ion, and the width of the $i$-th energy level is given by the following expression.
\[
\Delta v_i^R(T) = \tilde{a}_i \left( \frac{T}{\Theta_D} \right)^\gamma \int_0^{\theta_0/T} \frac{x^6 e^x}{(e^x - 1)^2} \, dx ,
\]

where \(x = h\omega/kT\), \(\tilde{a}_i\) is the coupling coefficient for the phonon–ion interaction and \(\Theta_D\) is the effective Debye temperature of the phonon distribution. Equation (1) can now be written in the following form:

\[
\Delta v_i(T) = \Delta v_i^{\text{strain}} + \sum_{j<i} \beta_{ij} + \Delta v_i^D(T) + \Delta v_i^M + \Delta v_i^R(T).
\]

At \(T = 0\) K, \(\Delta v_i = \Delta v_i^{\text{strain}} + \sum_{j<i} \beta_{ij} + \Delta v_i^M = \Delta v_{i0}\). \(\Delta v_{i0}\) represents the net contribution due to the random crystal strains, the temperature-independent spontaneous one-phonon and the temperature-independent multiphonon emission processes, and is called the residual width of the \(i\)-th level. In Eqs. (1) and (3), the width due to crystal strains is inhomogeneous broadening with Gaussian lineshape and the other terms give rise to homogeneous broadening with Lorentzian lineshape. Therefore, the simple summation in these equations gives only a rough approximation. A lineshape composed of both homogeneous and inhomogeneous parts can be represented by a Voigt profile [18]. The linewidth may be resolved into homogeneous and inhomogeneous contributions by using the numerical tables prepared by Posener [19].

Although the temperature-dependent part of the direct one-phonon process has been neglected by many authors [11 to 17] to describe their experimental data, the contribution of this process to the linewidth in the temperature range of our interest is significant and cannot be neglected. Therefore, we have included the contribution of the direct one-phonon process to the temperature-dependent spectral width in our analysis. The total contribution to the linewidth due to microscopic strain, spontaneous one-phonon, and multiphonon emission processes is assumed to be temperature independent. The temperature-dependent spectral width \(\Delta v(T)\) of the line is the sum of the energy spread of the two Stark energy levels involved in that particular transition, and can be written in the following form [12]:

\[
\Delta v(T) = \Delta v_0 + \sum_{j<i} \tilde{\beta}_{ij} \frac{1}{e^{\Delta E_i/kT} - 1} + \sum_{j>i} \tilde{\beta}_{ij} \frac{1}{e^{\Delta E_j/kT} - 1} + \sum_{j<f} \tilde{\beta}_{j\bar{f}} \frac{1}{e^{\Delta E_{\bar{f}}/kT} - 1} + \sum_{j>f} \tilde{\beta}_{j\bar{f}} \frac{1}{e^{\Delta E_{j}/kT} - 1} + \tilde{a} \left( \frac{T}{\Theta_D} \right)^\gamma \int_0^{\theta_0/T} \frac{x^6 e^x}{(e^x - 1)^2} \, dx ,
\]

where \(\tilde{\beta}_{ij}\) and \(\tilde{\beta}_{j\bar{f}}\) are the coupling coefficients for the ion–phonon interaction; \(E_i\) and \(E_f\) represent the initial and terminal energy levels, and \(E_j\) represents the intermediate energy level responsible for the phonon absorption or emission processes; \(\Delta v_0\) is the temperature-independent residual linewidth of the transition between two levels and due to random crystal strain and spontaneous one-phonon and multiphonon emission processes. The residual linewidth (\(\Delta v_0\)) was estimated by extrapolating the experimental linewidth data to \(T = 0\) K, and found to be 29.8 and 9.8 cm\(^{-1}\) for the \(R1 \to X_5\) and \(R1 \to Y_2\) transitions, respectively. For the initial level \(R1\), there is only one possible direct one-phonon absorption process \((R1 \to R2)\) for both the \(R1 \to X_5\) and \(R1 \to Y_2\)
transitions. Therefore, the second term in Eq. (4) is zero for these transitions. It is difficult to determine all the coupling coefficients of $b_{ij}$ and $b_{jf}$. Therefore, for the terminal level $X_5$, we consider only $X_5 \rightarrow X_4$ one-phonon emission process and neglect the others ($X_5 \rightarrow X_3, X_2, X_1$) in the fourth term in Eq. (4). Since there is no possible one-phonon absorption for the terminal level $X_5$, the fifth term in Eq. (4) is zero. Therefore, the simplified theoretical temperature-dependent spectral width for the $R_1 \rightarrow X_5$ transition can be written as

$$\Delta \nu(T) = \Delta \nu_0 + \tilde{\beta}_{R_1 \rightarrow R_2} \frac{1}{e^{\Delta E_{R_1 \rightarrow R_2}/kT} - 1} + \tilde{\beta}_{X_5 \rightarrow X_4} \frac{1}{e^{\Delta E_{X_5 \rightarrow X_4}/kT} - 1} + \bar{\alpha} \left( \frac{T}{\Theta_D} \right)^7 \frac{T}{(e^x - 1)^2} \, dx,$$

(5)

where $\tilde{\beta}_{R_1 \rightarrow R_2}, \tilde{\beta}_{X_5 \rightarrow X_4}, \bar{\alpha}$, and $\Theta_D$ are treated as adjustable parameters to obtain the best fit to the experimental linewidth data.

Let us now consider the $R_1 \rightarrow Y_2$ transition. Since it is difficult to determine all the values of $b_{ij}$ and $b_{jf}$, for the terminal level $Y_2$, we consider only $Y_2 \rightarrow Y_3$ one-phonon absorption process and neglect others ($Y_2 \rightarrow Y_4, Y_5, Y_6$) in the fifth term of Eq. (4). There is only one possible one-phonon emission process from the terminal level $Y_2(Y_2 \rightarrow Y_1)$ in the fourth term of Eq. (4). Therefore, the simplified temperature-dependent spectral linewidth for the $R_1 \rightarrow Y_2$ transition can be written as

$$\Delta \nu(T) = \Delta \nu_0 + \tilde{\beta}_{R_1 \rightarrow R_1} \frac{1}{e^{\Delta E_{R_1 \rightarrow R_1}/kT} - 1} + \tilde{\beta}_{Y_2 \rightarrow Y_3} \frac{1}{e^{\Delta E_{Y_2 \rightarrow Y_3}/kT} - 1} + \tilde{\beta}_{Y_2 \rightarrow Y_1} \frac{1}{e^{\Delta E_{Y_2 \rightarrow Y_1}/kT} - 1} + \bar{\alpha} \left( \frac{T}{\Theta_D} \right)^7 \frac{T}{(e^x - 1)^2} \, dx,$$

(6)

Table 1
Some experimental linewidth and line shift data and fitting parameters for the $R_1 \rightarrow X_5$ and $R_1 \rightarrow Y_2$ transitions of Nd$^{3+}$ in YLF

<table>
<thead>
<tr>
<th>transition</th>
<th>experimental</th>
<th>fitting parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>linewidth $\Delta \nu$ (cm$^{-1}$)</td>
<td>line shift $\delta \nu$ (cm$^{-1}$)</td>
</tr>
<tr>
<td></td>
<td>10 K</td>
<td>300 K</td>
</tr>
<tr>
<td>$R_1 \rightarrow X_5$</td>
<td>29.8</td>
<td>38.3</td>
</tr>
<tr>
<td>$R_1 \rightarrow Y_2$</td>
<td>9.8</td>
<td>18.3</td>
</tr>
<tr>
<td></td>
<td>$\Theta_D$ (K)</td>
<td>$\bar{\alpha}$ (cm$^{-1}$)</td>
</tr>
<tr>
<td>$R_1 \rightarrow X_5$</td>
<td>460</td>
<td>110</td>
</tr>
<tr>
<td>$R_1 \rightarrow Y_2$</td>
<td>460</td>
<td>90</td>
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where $\tilde{\beta}_{R_1 \rightarrow R_2}$, $\tilde{\beta}_{Y_2 \rightarrow Y_1}$, $\tilde{\alpha}$, and $\theta_D$ are treated as adjustable parameters to obtain the best fit to the experimental linewidth data. The thermal broadening due to the direct one-phonon, multiphonon relaxation, and Raman phonon scattering processes is homogeneous and therefore yields a Lorentzian lineshape in the temperature range investigated. The measured linewidths for the $R_1 \rightarrow X_5$ and $R_1 \rightarrow Y_2$ transitions are plotted as a function of temperature in Figs. 6 and 7, respectively. The circles represent the experimental results and the solid curves are the theoretical fittings. The experimental data were best fitted to Eqs. (5) and (6) with the fitting parameters $\tilde{\beta}_{R_1 \rightarrow R_2} = 0.05 \text{ cm}^{-1}$, $\tilde{\beta}_{X_5 \rightarrow X_4} = 0 \text{ cm}^{-1}$, $\theta_D = 460 \text{ K}$ and $\tilde{\alpha} = 110 \text{ cm}^{-1}$ for the $R_1 \rightarrow X_5$ transition, and $\tilde{\beta}_{R_1 \rightarrow R_2} = 0.05 \text{ cm}^{-1}$, $\tilde{\beta}_{Y_2 \rightarrow Y_3} = 0.2 \text{ cm}^{-1}$, $\tilde{\beta}_{Y_2 \rightarrow Y_1} = 0.1 \text{ cm}^{-1}$, $\theta_D = 460 \text{ K}$ and $\tilde{\alpha} = 90 \text{ cm}^{-1}$ for the $R_1 \rightarrow Y_2$ transition. These values are given in Table 1. The values of these parameters, along with Eqs. (5) and (6), can be used to recalculate the spectral linewidths (FWHMs) for both transitions. A measure of the accuracy of the fit is given by the rms deviation of the FWHMs [20]. We have obtained the rms deviations of 0.17 and 0.24 cm$^{-1}$ for the $R_1 \rightarrow X_5$ and $R_1 \rightarrow Y_2$ transitions, respectively. The respective rms linewidths are 32.52 and 12.86 cm$^{-1}$. The ratio of the rms deviation and
the rms linewidth yields an rms error less than 2% in both cases. It is worth noting that the sensitivity of the theoretically fitted curves is due to small changes in the values of the fitting parameters: $\beta$ and $\alpha$ were tested and found that they are more sensitive at higher temperatures than at lower temperatures. No attempt was made to test the sensitivity for change in the value of $\theta_D$, because its value was set equal to 460 K in all cases.

The line position of the $R_1 \rightarrow X_5$ transition was found to shift toward the shorter wavelength, whereas the $R_1 \rightarrow Y_2$ transition line shifted toward the longer wavelength as the crystal temperature was increased from 10 to 300 K. The temperature-dependent line positions of these transitions are shown in Fig. 8. According to the phonon-dependent line positions theory [13 to 18] the thermal shift of a given transition is due to stationary effects of the phonon–ion interaction. In order to compare the thermal shift of the sharp fluorescence line, it is assumed that the thermal shift of a spectral line is the algebraic sum of the shifts of the two levels involved in the transitions. Therefore, the simplified theoretical expression for the line shift can be written in the following form [11]:

$$
\delta \nu(T) = \delta \nu_0 + \alpha \left( \frac{T}{\theta_D} \right)^4 \theta_D T \int_0^{\theta_D/T} \frac{x^3}{e^x - 1} \, dx,
$$

where $\delta \nu_0$ (in cm$^{-1}$) = $\nu(0 \text{ K}) - \nu(10 \text{ K})$ and $\nu(0 \text{ K})$ was obtained by extrapolating the experimental line position data to 0 K. For the $R_1 \rightarrow Y_2$ transition, $\delta \nu_0$ was estimated to be 0 cm$^{-1}$ from Fig. 8.

The average line shifts for the $R_1 \rightarrow Y_2$ transition are plotted as a function of temperature in Fig. 9. The measured line shifts have been fitted to Eq. (7) with the fitting parameters of $\theta_D = 460 \text{ K}$, $\alpha = 23.5 \text{ cm}^{-1}$, and $\delta \nu_0 = 0 \text{ cm}^{-1}$ for this transition. These values are given in Table 1. As mentioned earlier, each measurement was repeated.

![Fig. 9](image-url)
three times; the error bars for the measured data are also shown in Fig. 9. It is important to note that for the linewidths of the $R_1 \rightarrow X_5$ and $R_1 \rightarrow Y_2$ transitions, the best theoretical fittings to Eqs. (5) and (6), respectively, were obtained with $\theta_D = 460$ K which is also the same as the Debye temperature obtained for the best fitting of the temperature-dependent line shift for the $R_1 \rightarrow Y_2$ transition, and an excellent agreement between the theoretical and experimental results is obtained over the entire temperature range after including the temperature-dependent direct one-phonon process to Eq. (4). Therefore, it can be concluded that the temperature-dependent part of the one-phonon process is of importance for the temperature dependence of linewidths in Nd$^{3+}$ : YLF.

4. Summary and Conclusion

Using the room-temperature fluorescence spectra for the $^4F_{3/2} \rightarrow ^4I_{9/2}$ and $^4F_{3/2} \rightarrow ^4I_{11/2}$ intermanifold transitions of Nd$^{3+}$ in YLF, a detailed Stark component characterization has been performed. A computer program written in C was used to obtain the energy level diagrams of these multiplets. The accuracy of the arrangements of energy levels for the corresponding inter-Stark transitions in both energy level diagrams (Figs. 3 and 4) are found to be in excellent agreement with the obtained rms errors of less than 2.0 in both cases.

In addition, using the well-resolved fluorescence spectra of the $^4F_{3/2} \rightarrow ^4I_{9/2}$ and $^4F_{3/2} \rightarrow ^4I_{11/2}$ transitions of Nd$^{3+}$ in YLF laser host, the widths, positions, and shifts of the sharp lines of the respective $R_1 \rightarrow X_5$ and $R_1 \rightarrow Y_2$ inter-Stark transitions have been investigated as a function of temperature. The low-temperature linewidth for the $R_1 \rightarrow X_5$ transition is 29.8 cm$^{-1}$ and for the $R_1 \rightarrow Y_2$ transition is 9.8 cm$^{-1}$. The $R_1 \rightarrow X_5$ transition line has a broader residual width than the $R_1 \rightarrow Y_2$ transition line. This finding can be explained by the fact that the spontaneous one-phonon emission $X_5 \rightarrow X_4, X_3, \ldots X_1$ processes could contribute significantly to the linewidth of this transition.

The linewidths of the $R_1 \rightarrow X_5$ and $R_1 \rightarrow Y_2$ transitions were both found to increase by 8.5 cm$^{-1}$, as the temperature was increased from 10 to 300 K. The experimental results have been quantitatively verified by the existing phonon–ion interaction theory which assumes a Debye phonon distribution in solids. For the linewidths of the $R_1 \rightarrow X_5$ and $R_1 \rightarrow Y_2$ transitions, the best theoretical fittings to Eqs. (5) and (6), respectively, were obtained with the same Debye temperature of $\theta_D = 460$ K. It is important to note that the same Debye temperature was obtained for the best fitting of the temperature-dependent line shift for the $R_1 \rightarrow Y_2$ transition. Within the experimental uncertainties, excellent agreements between the theoretical and measured values are obtained over the entire temperature range investigated after including the temperature-dependent direct one-phonon process to Eq. (4). Therefore, it may be concluded that the temperature-dependent part of the one-phonon process is of importance for the temperature dependence of Nd$^{3+}$ linewidths in YLF host. The accuracies of the fittings of the experimental linewidth data with the theoretical model have been measured by calculating the rms deviations and the rms errors which are less than 2% in both the $R_1 \rightarrow X_5$ and $R_1 \rightarrow Y_2$ transitions. The error bars for experimental points are shown in all cases. It is worth noting that the sensitivity of the theoretical curves to small changes in the values of the adjustable parameters $\beta$ and $\alpha$ have been also tested.
and found that the sensitivity at higher temperature is much more pronounced than at lower temperatures. For example, a change of 10% of the values of \( \beta \) produce a change in the final linewidth curve for the \( R_1 \rightarrow Y_2 \) transition by only 0.17 cm\(^{-1} \) at 300 K and exhibits almost no change in the final curve at 10 K. Likewise, a change of 10% of the values of \( \alpha \) result in a change of the same curve by only 0.67 cm\(^{-1} \) at 300 K and shows an insignificant change in the final curve at 10 K.

At very low temperatures, the linewidths can be considered as residual and are mainly due to random crystal strains, spontaneous one-phonon and multiphonon emission processes. According to Chen and Di Bartolo [12], at temperatures below 80 K in Nd:GSGG system, the temperature-dependent part of the direct one-phonon processes played an important role, but became insignificant as temperature was increased beyond 80 K, when the Raman phonon scattering processes became highly dominant [12]. It is believed that the temperature-dependent contribution to the linewidth due to one-phonon processes might contribute significantly in the case of rare earth ions in crystalline hosts, since there are many Stark levels with small energy separations which can be easily bridged by one-phonon absorption or emission. Our investigation shows that the direct one-phonon processes contribute significantly to the temperature-dependent linewidth of Nd\(^{3+} \) in YLF in the temperature range of our interest. When the direct one-phonon process is included in the theoretical expression of the temperature-dependent linewidth, we have achieved better fittings of the experimental linewidth data.

In general, the sharp spectral lines in crystalline solids are observed to shift toward the longer wavelengths with increasing crystal temperature. The red-shift of the 1052.4 nm line was fitted well with the theoretical expression given by Eq. (7), while the blue-shift of the 908 nm line with increasing temperature could not be fitted with the available theoretical expressions. Nevertheless, the blue-shift has been observed in several laser crystal hosts. For example, the same Nd\(^{3+} \) transition in YAG [13] and GSGG [12] hosts was found to shift to the shorter wavelength (blue-shift). The blue-shift of the \( R_1 \rightarrow X_5 \) transition may be attributed to the lowering of the terminal level \( X_5 \), the uppermost Stark-level of the \( ^4I_{15/2} \) manifold, due to the downward pushing by the upper Stark levels of the \( ^4I_{11/2} \) manifold [13]. Since the downward movement of the \( X_5 \) level with increasing temperature is not clear at this time, further studies on this and other potential laser hosts are needed in order to have a better understanding of the physical mechanisms of the blue-shift.

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References