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The Temperature-Dependence of Multiphonon Relaxation of Rare-Earth Ions in Solid-State Hosts

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Abstract

Rare-earth ions are used in a wide range of emissive devices – ranging from lasers to displays – where high optical efficiency and narrow-linewidth are important. While their radiative properties are important, nonradiative properties are also critical since they can reduce optical efficiency and generate heat. In this paper, theories for multiphonon relaxation rate are reviewed for rare-earth excited states in solid-state dielectric hosts. A range of various approaches are used to simplify the mathematical form of the rate equations. The $^2H_{9/2}$ excited state of Er^{3+} , responsible for a technologically significant green emission, is modeled to show how the various theories manifest an order-of-magnitude variation in the thermal dependence of the multiphonon relaxation rate, as well as anomalous local minima in phonon scattering for temperatures above 0 K. This work proposes a corrective term of two quanta ($\nu = +2$) of the mediating phonon energy to energy gap, so the calculated and the experimentally determined relaxation rates are equal. Radiative quantum efficiencies of both the $^1G_4 \rightarrow ^3H_5 \sim 1.3 \mu m$ and $^3F_3 \rightarrow ^3F_2 \sim 7 \mu m$ of Pr^{3+} are calculated to show the importance of both proper measurement of phonon energy and application of the multiphonon relaxation rate theory.

Graphical abstract

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I. INTRODUCTION

The increasing importance of advanced solid-state laser systems requires more and accurate information about the rate of nonradiative relaxation (NR) processes. Such NR processes, generally including concentration quenching, cross-relaxation and multiphonon emission, are necessary to complete the overall radiative emissions (ranging from ultraviolet to infrared) of rare-earth (RE) ‘activator’ centers.¹ In practice, the effects of these NR processes limit the achievable quantum efficiency (QE) of the luminescent system, which determines the necessary pump power and other design considerations.² For a host activated by a dilute RE dopant concentration, the total NR rate is only determined by the multiphonon emission rate, W_{NR} .³ The radiative QE, η , can be computed for an optical transition between an initial excited-state manifold, i , and a final manifold, j , as follows

$$\eta = \frac{\tau_m}{\tau_i} = \frac{\sum_j A_{i,j}}{\sum_j A_{i,j} + W_{NR}}, \quad (1)$$

where τ_m is the experimentally measured lifetime of i excited state, and τ_i is theoretical radiative lifetime. The efficiency is the probability of the total radiative transition rate from

the initial i energy level to the lower-lying j levels, $\sum_j A_{i,j}$, normalized to the overall

depopulation rate of the excited state, $\sum_j A_{i,j} + W_{NR}$. Maximizing η is typically achieved by minimizing W_{NR} . Hence, significant implications can be technologically derived from Eq.

(1). Defining β as $\frac{W_{NR}}{\sum_j A_{i,j}}$, the η and its first derivative with respect to β are $\eta(\beta) = \frac{1}{1+\beta}$

and $\left| \frac{d\eta(\beta)}{d\beta} \right| = \frac{1}{(1+\beta)^2}$, respectively. Figure 1 shows that as the β value approaches zero, the uncertainty in W_{NR} increases. This uncertainty ultimately leads to large errors in the

computation of η . Thus, to ensure proper quantitative evaluation of QE, an accurate determination of W_{NR} is imperative.

Theories and mathematical descriptions for nonradiative decay of RE excited states were first proposed in the 1960s on the basis of an approximated dynamic crystal field potential around RE ‘activator’ (perturbed by lattice vibration).⁴ Thermal dependence of the relaxation rate correlates to an integral number of monoenergetic phonons with the maximum vibrational energy of the host. In the early 1970s, Fong *et al.* presented a more complete relaxation rate theory by associating both thermal and electronic band gap dependence of the multiphonon emission with five phonon-scattering (Fong-model).^{5,6} Yet the approximations made decades ago are still routinely used to quantify nonradiative relaxation because it is far simpler to do than the complex mathematical modeling required for the Fong-model.^{7–11} Although there is a good correlation between theoretical and experimental energy level dependencies for nonradiative decay rates, these approximations have been known to create meaningless nonphysical trends, which will be discussed later.

In this paper, we outline the multiphonon relaxation theories and their approximations, reveal the nonphysical behavior induced from the incorrect application of simplified equation, and provide a corrective term that achieves better agreement between the relaxation rates calculated by theoretical and experimental treatments. Promoted by interest for visible to infrared light sources, the multiphonon relaxation rates of $\text{Er}^{3+}: {}^2\text{H}_{9/2}$, $\text{Pr}^{3+}: {}^1\text{G}_4$ and $\text{Pr}^{3+}: {}^3\text{F}_2$ excited states in lanthanum halides (LaF_3 and LaCl_3) are calculated as a function of temperature within the framework of more comprehensive and approximate approaches, respectively. LaF_3 and LaCl_3 are specified as representative hosts due to their low phonon energies ($\hbar\omega_{\text{LaF}_3} \sim 350 \text{ cm}^{-1}$, $\hbar\omega_{\text{LaCl}_3} \sim 260 \text{ cm}^{-1}$, as listed in Table 1)⁶ and their exceptional transparency at shorter wavelengths.

II. REVIEW OF MULTIPHONON RELAXATION MODELS

A. Approximations based on a single mediating phonon

The 4f electrons of RE species are relatively well-shielded by the 5s and 5p electrons such that RE ions only are weakly coupled to the crystal field.¹² Despite this lessened degree of interaction, perturbations in the ligand field caused by lattice vibrations promote the 4f electronic transitions from an excited state to one lowered by lattice mode energy.¹³ When energy differences between the adjacent levels are greater than the maximum phonon energy ($\hbar\omega_{\text{max}}$, where $\hbar$ is Planck constant, and ω_{max} is the maximum phonon frequency), higher order processes (i.e., multiphonon emission) are required by conservation laws. In the weak coupling limit between the RE and its host,^{7,13} the interaction Hamiltonian, H , is given by expanding the static crystal field potential, V_0 , in a Taylor series around the ionic equilibrium position

$$H = V_0 + \sum_i V_i Q_i + \sum_{ij} V_{ij} Q_i Q_j + \dots, \quad (2)$$

where Q_i are the normal mode coordinates of the host lattice, and V_{ij} are derivatives of the crystal field with respect to their coordinates, (i, j).

Single phonon transition rates involve matrix elements of the modes that couple to RE through the second term of Eq. (2). Taking this single-phonon term in the expansion of a p-order perturbation calculation (p is the quantum-mechanical momentum operator) yields a very complicated function. This function sums over the matrix elements for all 2^{p-1} sequences of intermediate electronic states normalized to the number of single phonons with

energy $\hbar\omega = \frac{\Delta E}{p}$. This energy is what is required to bridge the energy difference between the two given electronic transition levels. Assuming that each matrix element can be replaced by an average value, $\langle a|V'|b \rangle$, the multiphonon relaxation rate relative to the energy gap to be bridged, W_{NR} , can be written as the comparison of the decay rate for a p-phonon process with that for a p-1 phonon decay,⁷

$$W_{NR} = \frac{2\pi}{\hbar} \left(\frac{\hbar}{2M\omega} \right)^p (n+1)^p 2^{2(p-1)} m^{2p} \frac{|\langle a|V'|b \rangle|^{2p}}{(\hbar\omega)^{2(p-1)}}, \quad (3)$$

where m is the number of oscillators coupled to the ion, n is the phonon occupation number (discussed below), M is the reduced mass of the vibrating ionic system of m coupled oscillators, a and b refer to the different intermediate electronic states, and $|V'|$ is the average crystal field. The temperature dependence of multiphonon emission rate arises from the dependence of phonon mode on Bose-Einstein occupation number $n(T)$,^{7,12}

$$n(T) = \left(e^{\frac{\hbar\omega}{kT}} - 1 \right)^{-1}, \quad (4)$$

where kT is Boltzmann energy with $k = 0.695 \text{ cm}^{-1}/\text{K}$. Therefore, for a p-order process, the $(n+1)^p$ temperature dependence identifies the order and the energy of mediating phonon. The rate dependence on energy gap results from comparing the rate for p- with that for (p-1)-phonon process. As the host material remains constant, that is $\hbar\omega$, m, and $\langle a|V'|b \rangle$ are constants, the Eqn. 3 simplifies directly to Eqn. 5 when one divides $W_{NR}(p)$ by $W_{NR}(p-1)$:

$$\frac{W(p)}{W(p-1)} = 4m^2 \left(\frac{\hbar}{2M\omega} \right) (n+1) \frac{|\langle a|V'|b \rangle|^2}{(\hbar\omega)^2}, \quad (5)$$

Owing to the weak coupling between the RE and its crystal field, the multiphonon emission

rate is $\frac{W(p)}{W(p-1)} = e^\epsilon$, where ϵ is the electron-phonon coupling constant, a value much less than 1.⁴ Resultantly the rate for a pth-order process is approximated by⁴

$$W^{(p)} \approx A\varepsilon^p = A \exp \left[\frac{\ln(\varepsilon)}{\hbar\omega} \right] \Delta E, \quad (6)$$

where A is a constant. On the basis of the initial assumption that the lowest-order process is responsible for the relaxation, this order is approximately determined by the minimum

number of highest energy host phonons required to bridge the energy gap, $p \approx \frac{\Delta E}{\hbar\omega_{\max}}$.

Making use of the above equations and defining ε in terms of $\alpha = -\frac{\ln(\varepsilon)}{\hbar\omega}$, the multiphonon emission rate becomes temperature-independent⁴

$$W = Ce^{\alpha\Delta E}, \quad (7)$$

where C and α ($\alpha < 0$) are constant characteristic of the RE host lattice. These results were discussed in far greater detail by *Riseberg and Weber*¹⁴ and *Reisfeld*.¹⁵ With increasing temperature, the phonon emission will be stimulated by thermal phonons and the relaxation rate, W, increases according to⁴

$$W(T) = W(0)[1 + \bar{n}(T)]^p, \quad (8)$$

where $\bar{n}(T)$ is the average occupation number of maximum phonon energy $\hbar\omega_{\max}$, which follows a Bose distribution

$$\bar{n}(\hbar\omega_{\max}) = \frac{1}{e^{\frac{\hbar\omega_{\max}}{kT}} - 1}, \quad (9)$$

By combining the temperature independent Eq. (7) and the temperature dependence approximated by Eqs. (8) and (9), the simplified multiphonon relaxation rate is given by¹⁶

$$W_{NR} = Be^{\alpha\Delta E} \left\{ 1 - e^{-\frac{\hbar\omega_{\max}}{kT}} \right\}^{-\frac{\Delta E}{\hbar\omega_{\max}}}, \quad (10)$$

The above derivation of Eq. (10) is called as the Reisfeld-model. The relative NR parameters like B and α are given for a variety of crystals are summarized in Table 2.

B. Modified approximation for $\text{LaF}_3:\text{Er}^{3+}$ by Riseberg et al

In practice, Eq. (10) can be taken a further step to include contributions from the Stark levels (i.e., the inner structure or multiplicities).⁴ In these cases, Eq. (10) is modified to include a

term that accounts for the number and relative energy difference between sublevels with respect to the thermal distribution. For the multiphonon transition from the $^2H_{9/2}$ to $^4F_{3/2}$ of Er^{3+} in LaF_3 , Riseberg *et al.* modeled the temperature dependence of multiphonon relaxation rate (sec^{-1}) of $Er^{3+}: ^2H_{9/2} \rightarrow ^4F_{3/2}$. In this case, thermal depopulation of higher-lying Stark levels accounted for the assumption of three nondecaying energy levels 200 cm^{-1} above the lowest energy level.⁴ This is expressed as follows:

$$W_{NR} = 1.1 \times 10^4 \left\{ 1 - e^{-\frac{310}{kT}} \right\}^{-6} \left\{ 1 + 3e^{-\frac{200}{kT}} \right\}^{-1}, \quad (11)$$

where the 1.1×10^4 is the temperature-independent prefactor that includes contributions from the appropriate C and α constants in Eq. (7) for LaF_3 host material and the energy difference ($\sim 1860\text{ cm}^{-1}$) between the $^2H_{9/2}$ and $^4F_{3/2}$ states of Er^{3+} .

The great utility of Eq. (10) and the modified version of Eq. (11) are that they both permit the determination of multiphonon relaxation rates through quantities that are fairly easy to measure. First, the energy gap, E , can be measured by either absorption spectroscopy or found in the literature for the more common host materials (i.e., see Ref. 18). Second, the phonon energy, $\hbar\omega$, can be measured by either Raman or phonon sideband spectroscopy.¹⁹ Finally, the material constants, C and α can be quantified by curve-fitting the nonradiative decay rate from the high-lying energy states with differing E to adjacent states of RE ions. The relative ease of these measurements renders Eq. (10) and Eq. (11) as the preferred approaches to determine W_{NR} .

C. Adiabatic approximation derived by Fong *et al*

In the early 1970s, Fong *et al.*^{5,6} derived a more complete theory of nonradiative relaxation as a function of temperature and energy level difference without many approximations (the Fong-model). The investigation into the multiphonon relaxation rate of RE-doped solids made use of the Born-Oppenheimer (BO) adiabatic approximation, dealing with the separation of a system's wavefunction into 'faster' electronic processes and 'slower' nuclear ones.²⁰⁻²³ Accordingly, the kinetic energy operator for the lattice can be regarded as a small perturbation on the electronic wavefunction. More specifically, electronic energies, e_α , of the zeroth-order BO eigenstates, $|\alpha\rangle$, are written parametrically in terms of the normal mode coordinates of lattice phonons. In terms of the phonon creation and annihilation operators, the electron-lattice Hamiltonian can be expressed as⁵

$$H = -\frac{\hbar^2}{2m} \sum_i \frac{\partial^2}{\partial r_i^2} + V(\mathbf{r}, \mathbf{R}) - \frac{\hbar^2}{2} \sum_j \frac{\partial^2}{M_j \partial R_j^2}, \quad (12)$$

where M_j is the j th normal mode of effective mass, and $\mathbf{r}$ and $\mathbf{R}$ are the coordinates of electrons and lattice phonons, respectively, and $V(\mathbf{r}, \mathbf{R})$ includes all electrostatic interactions (e.g., electron-ion and ion-ion). The Schrödinger equation then takes the form,

$$H|\alpha(\mathbf{r}, \mathbf{R})\rangle = \varepsilon_{\alpha}(\mathbf{R})|\alpha(\mathbf{r}, \mathbf{R})\rangle, \quad (13)$$

At the zeroth order, the problem would simplify to solving the Schrödinger equation, where eigenvalues are expanded in power series of the ionic displacements from equilibrium. This is due to the dynamic nature of the lattice, a similar treatment to that given in Eq. (2) with respect to static crystal field potentials. Using the weak coupling limit, a saddle-point approximation enabled Fong *et al.* to show that time integration of the correlation function leads to a relaxation rate in which the energy gap is effectively modified by the addition or subtraction of ν quanta of the mediating phonon mode via five contributing scattering processes.^{13,24,25} The radiationless decay rate of electronically excited ions in a crystalline lattice is given by⁶

$$W_{\alpha\alpha'} = \frac{(2\pi)^{1/2}}{\hbar^2} L_m |C_{\alpha\alpha'}|^2 \omega_m^{-1} \sum_{\Delta\nu=-2}^{\Delta\nu=+2} \lambda_{\Delta\nu} (p - \Delta\nu)^{-1/2} \times \exp \left[-\frac{1}{4} L_m g_m^2 (2n_m + 1) \right] \times \exp \left\{ -(p - \Delta\nu) \left[\ln \left(\frac{4(p - \Delta\nu)}{L_m g_m^2 (n_m + 1)} \right) - 1 \right] \right\}, \quad (14)$$

where $p = \frac{\Delta E}{\hbar\omega} = \frac{(\varepsilon_{\alpha} - \varepsilon_{\alpha'})}{\hbar\omega}$, L_m is an effective degeneracy factor, n_m is the phonon occupation number for the effective L_m -fold degenerate mode m mediating the relaxation, g_m^2 is a (dimensionless) displacement factor related to phonon creation and annihilation operators, $|C_{\alpha\alpha'}|^2$ is the electron-phonon coupling constant and the $\lambda_{\nu=-2,\dots,+2}$ coefficients are defined as:

$$\begin{aligned} \lambda_{-2} &= \frac{1}{4} L_m g_m^2 n_m^2 \\ \lambda_{-1} &= -\frac{1}{2} L_m g_m^2 (2n_m + 1) n_m + n_m \\ \lambda_0 &= \frac{1}{4} L_m g_m^2 [6n_m(n_m + 1) + 1] \\ \lambda_{+1} &= -\frac{1}{2} L_m g_m^2 (2n_m + 1)(n_m + 1) + n_m + 1 \\ \lambda_{+2} &= \frac{1}{4} L_m g_m^2 (n_m + 1)^2 \end{aligned}, \quad (15)$$

All of the above terms are determined through least-squares fitting of experimental rates as function of temperature and energy gap difference. Furthermore, by assuming only one mode dominates the RE $\Leftrightarrow$ lattice coupling (i.e., weak-coupling limit),^{24–26} the relaxation rate comprises five contributions that correspond to the scattering-related addition or subtraction of ν quanta of the mediating phonon energy to the transitional energy gap, $\varepsilon_{\alpha} - \varepsilon_{\alpha'}$.

$$\varepsilon_{\alpha} - \varepsilon_{\alpha'} - \Delta\nu \hbar\omega_m > L_m g_m^2 \hbar\omega_m, \quad (16)$$

As a consequence, determination of the relaxation rate would follow from time integration²⁵ in the weak-coupling limit by the saddle-point approximation.²⁴ Table 1 lists the corresponding parameters for LaF₃ and LaCl₃ host materials.^{5,6}

III. QUANTITATIVE COMPARISON BETWEEN MODELS, UNIFICATION AND RESULTS

A. Inaccuracy induced by rough employment of $W_{NR}^{Fong}(T)$ and $W_{NR}^{Reisfeld}(\Delta E)$

In practice, it is obvious that inaccuracy would be induced by simply employing the different models of $W_{NR}(T)$ and $W_{NR}(\Delta E)$, respectively. In the low-temperature limit ($kT \ll \hbar\omega_{max}$), Eq. (14) can be reduced to

$$W_{NR}^{Fong}(T) = W_{NR}(T=0) \left[1 + pe^{-\frac{\hbar\omega_{max}}{kT}} \right], \quad (17)$$

which is functionally similar to that of Eq. (10), $W_{NR}^{Reisfeld}(\Delta E)$. However, at higher temperatures when $kT \sim \hbar\omega_{max}$, the computed result of $W_{NR}^{Fong}(T)$ and that of $W_{NR}^{Reisfeld}(\Delta E)$ would differ significantly from each other. For instance, for LaF₃ host lattice with $\hbar\omega_{max} = 350 \text{ cm}^{-1}$, the ratio of Eq. (10) to Eq. (16) at $T=100 \text{ K}$ is essentially unity for equal $W_{NR}(T=0)$, while, at $T=300 \text{ K}$, the ratio becomes > 2 , invalidating the approximation. Thus, great calculation must be taken when using these approximations.

B. Inconsistent multiphonon relaxation rates and non-physical trends

In order to clearly illustrate the possible inaccuracies, the temperature dependence of relaxation rate, $W(T)$, for a given $^2H_{9/2} \rightarrow ^4F_{3/2}$ transition of Er^{3+} is comparatively calculated through the three models of Eqs. 10, 11 and 14. In practice, Fong's theory for a multiphonon rate, $W(T)_{NR}^{Fong}$, can be calculated from

$$W(T)_{NR}^{Fong} = \Gamma_{-2} + \Gamma_{-1} + \Gamma_0 + \Gamma_{+1} + \Gamma_{+2}, \quad (18)$$

where Γ_n ($n = -2, -1, 0, +1, +2$) is the individual contribution of each $W_{\alpha\alpha'}(\lambda_{\nu})$ effective phonon. All the parameters for nonradiative relaxation are provided in Tables 1 and 2. Figure 2 shows the multiphonon relaxation rate from the $^2H_{9/2}$ excited state to the following $^4F_{3/2}$ state of Er^{3+} in LaF₃. At room temperature, there is over an order-of-magnitude difference between curves because the $W(T)_{NR}$ values are estimated by curve-fitting experimental data using the more approximate model, $W_{NR}^{Riseberg}$, and the most rigorous model, W_{NR}^{Fong} . Accordingly, this discrepancy greatly influences the computation of η , the radiative quantum efficiency. This is especially pronounced in the case of multiphonon relaxation with a relatively large energy gap, such as for the 2545 cm^{-1} emission from the 1G_4 level to the 3F_4 level for Pr^{3+} in LaF₃. At room temperature, a difference of 400% in the radiative QE of

the $^1G_4 \rightarrow ^3H_5$ transition at about $1.3 \mu\text{m}$ can be obtained by using W_{NR}^{Riseberg} and W_{NR}^{Fong} calculation modes,²⁷ respectively.

Further inspection of the Riseberg-model [Eq. (11)] reveals another serious problem, namely the anomalous appearance of local minima. The problem is the anomalous appearance of local minima in the multiphonon emission rate at $T > 0 \text{ K}$ (Figure 3). The local minima have the physical basis to exist. The anomalous appearance solely results from the functional form of the mathematical simulation through the selection of fitting parameters, and lead to large errors. The problem is that it causes large errors in subsequently calculating the radiative QE. For instance, $\text{LaCl}_3:\text{Pr}^{3+}$ crystal is of great commercial interest for room temperature solid-state infrared sources and sensors.^{28–30} If the radiative properties of $\text{Pr}^{3+}: ^3F_3 \rightarrow ^3F_2$ at $7 \mu\text{m}$ are predicted by simply applying the Riseberg-model, the radiative QE of $\text{Pr}^{3+} \sim 7 \mu\text{m}$ calculated at 77 K (liquid nitrogen cooling) increases by a factor of 5 relative to that evaluated at temperature cooled from 300 to 150 K or below. In principle, extrapolation indicates that, for $\text{Pr}^{3+}: ^3F_3 \rightarrow ^3F_2$ in LaCl_3 , the point at 0 K features the minimum multiphonon relaxation rate of $1.1 \times 10^4 \text{ sec}^{-1}$, while the fitting of the Riseberg-model yields a minima of $1.046 \times 10^4 \text{ sec}^{-1}$ in the 77–150 K range.

C. Unification of various approaches

Given the inaccuracy and nonphysical behavior of the three models, it is worth investigating if a unification of the various approaches can resolve these problems. Equation (8) represents a relaxation rate comprising penta-phononic scattering, as opposed to the mono-phononic case of Eq. (6). The polyphonic scattering yields the greatest contribution to the overall NR process through the terms related to the addition of vibrational energy to the electronically excited ion. Since the $\lambda_{\nu} = +2$ term provides the largest perturbation to the mono-phononic mechanism in the Fong's approach,⁶ it is reasonable to suggest adding the Γ_{+2} to Eq. (10) as following

$$W_{NR} = B e^{\alpha \Delta E} \left\{ 1 - e^{-\frac{\hbar \omega_{\max}}{kT}} \right\}^{-p} + \frac{(2\pi)^{1/2}}{-\hbar^2} L_m |C_m|^2 \frac{\lambda_{+2}}{\omega_m (p-2)^{1/2}} \times \exp \left[-\frac{1}{4} L_m g_m^2 (2n_m + 1) \right] \times \exp \left\{ -(p-2) \left[\ln \left(\frac{4(p-2)}{L_m g_m^2 (n_m + 1)} \right) - 1 \right] \right\}, \quad (19)$$

All the terms in Eq. (19) are defined in the abovementioned sections, as listed in Table 1 and Table 2. As shown in Figure. 4(a), the large deviation between the results of the Reisfeld-model and that of the Fong-model can be eliminated by adding the Fong-model Γ_{+2} term to the Reisfeld-model (Figure 4(b)). Noted that the values listed in Table 1 for $L_m g_m^2$ and $L_m |C_m|^2$ are specifically for the $^2H_{9/2}$ state of Er^{3+} in LaF_3 because the multiphonon transition between RE electronic energy levels are just coupled to the different phonon modes.^{5,6} Extension to other RE transitions requires the specific parameters either previously tabulated or calculated using the outlined methodology. For clarity, the proposed addition to the

Reisfeld-model of multiphonon relaxation rates for $\text{LaF}_3:\text{Er}^{3+}$ and $\text{LaCl}_3:\text{Er}^{3+}$ are summarized below for the Reisfeld-model to Fong-model transition,⁵

$$F(T)_{\Gamma+2} = \frac{\left[\frac{1}{4}L_g(n(T)+1)^2\right] (p(E)-2)^{\frac{1}{2}} \cdot \exp\left[-\frac{1}{4}L_g(2n(T)+1)^2\right]}{\exp\left[-(p(E)-2) \cdot \left[\ln\left(\frac{4(p(E)-1)}{L_g(n(T)+1)}\right) - 1\right]\right]}, \quad (20)$$

For example, LaF_3 host material: $L_c = 7.356 \times 10^3$; $\frac{\sqrt{2}\pi}{\omega \cdot h^2} L_c = 1.12 \times 10^{13}$; $L_g = 0.1444$;

$p(E) = E/310$, and LaCl_3 host material: $L_c = 0.057$; $\frac{\sqrt{2}\pi}{\omega \cdot h^2} L_c = 1.006 \times 10^9$; $L_g = 0.1537$;
 $p(E) = E/238$.

D. Influence of selected transition energy

Although the specific focus of paper is on the discrepancies among the values of $W_{\text{NR}}(T)$ obtained from several models, there still exists potential ambiguity in the definition of energy difference, E , between the adjacent excited states of RE ions, ultimately effecting the QE calculation. Further work should be done before the applying extension of Fong's parameters to different E regimes. The Reisfeld-model [Eq. (10)] shows that the different values of E would lead to a wide range of $W_{\text{NR}}(T)$. For Pr^{3+} , the $^1\text{G}_4 \rightarrow ^3\text{H}_5$ at about 1.3 μm because of its potential use in the next-generation optical amplifier.^{28–32} The multiphonon relaxation rate of Pr^{3+} : $^1\text{G}_4$ state is calculated to be 112 sec^{-1} by Eq. (10), where the phonon energy and multiphonon relaxation parameters of LaF_3 are listed in Table 2. E of $^1\text{G}_4$ - $^3\text{F}_4$ of Pr^{3+} is conventionally determined by absorption spectroscopy and found to be 2966 cm^{-1} in terms of the manifold centroid value (e.g., the energetic average of Stark sublevels).³³ Correspondingly, the radiative QE is estimated as

$$\eta_{\text{LaF}_3:\text{Pr}^{3+}}(^1\text{G}_4 \rightarrow ^3\text{H}_5) \cong \frac{321}{321+112} \cong 74\%, \quad (21)$$

where 321 sec^{-1} is the spontaneous emission probability for the $^1\text{G}_4$ level of Pr^{3+} in LaF_3 as given by Weber.³⁴ However, a QE of 74% is approximately 500% larger than the value determined experimentally,^{29–31} or that expected based on the relatively small E ratio. The correct definition of E should take the specific intermanifold structure into account because the minimum energy difference would originate from the lowest Stark component of the excited state and the upper Stark component of the adjacent lowest lying energy level. Recalculation of the $^1\text{G}_4$ - $^3\text{F}_4$ E in this manner for LaF_3 yields a value of $\sim 2545 \text{ cm}^{-1}$.^{27,35} Accordingly, the multiphonon relaxation rate of Pr^{3+} : $^1\text{G}_4$ state is calculated to be 1323 sec^{-1} by Eq. (10), and then the QE is about 20%, which is much closer to those measured on LaF_3 : Pr^{3+} materials prepared by various methods.^{31,27,35}

For LaCl_3 , the multiphonon relaxation rate of Pr^{3+} : $^1\text{G}_4$ state is calculated to be $5.11 \times 10^{-6} \text{ sec}^{-1}$ by Eq. (10) and the theoretical QE for Pr^{3+} : $^1\text{G}_4 \rightarrow ^3\text{H}_5$ $\sim 1.3 \mu\text{m}$ is about 100%,

where the spontaneous emission probability for the 1G_4 level of Pr^{3+} in LaCl_3 is given to be 682.0 sec^{-1} .³⁶ Table 3 summarizes the calculated values for the $\text{Pr}^{3+} \sim 1.3 \mu\text{m}$ emission for the lanthanum halides.^{34,36} The negligibly small contributions to the $\sum_j A_{i,j}$ term in the

$$\eta = \frac{\sum_j A_{i,j}}{\sum_j A_{i,j}} = 1$$

denominator of Eq. (1) for η allows its reduction to 1. Obviously, this is the

case for any transition where $W_{\text{NR}} \ll \sum_j A_{i,j}$. It can be speculated that, with very low phonon energy, the great utility of these halides (chlorides) is the lack of phonon influence on the electronic transitions of RE^{3+} ions that do not possess large radiative emission probabilities in other hosts, such as oxides.^{3,28–31} In addition, halides are transparent over a much broader range than other infrared materials like the chalcogenides, which makes them more appropriate materials for active devices (e.g., UV, blue and green upconversion laser sources).

IV. CONCLUSIONS

A review of the multiphonon relaxation processes of RE excited states has been presented along with several approximation models, which are customarily applied to simplify its mathematical description so as to permit the evaluation of characteristic parameters with relative experimental ease. Temperature dependence of multiphonon relaxation rates for the $^2H_{9/2}$ state of Er^{3+} -doped LaF_3 were employed to show the significant difference by means of the typical Reisfeld-, Riseberg-, and Fong-model, respectively. Comparison of the three models gives insight to how the approximation leads to inaccuracies and the nonphysical existence of local minima in the magnitude of phonon scattering for temperature above absolute zero. A unified model with a corrective term was empirically derived to significantly improve the agreement between relaxation rates predicted using the various approximations by the measured and tabulated spectral absorption data. In addition, QE calculations can be corrected by defining the minimum energy difference of RE ions in the Stark manifold.

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Figure 1.

Quantum efficiency (η , black solid line) and its derivative ($\left|\frac{d}{d\beta}\eta(\beta)\right|$, red dash line) as a

function of $\beta \left(\frac{W_{NR}}{\sum_j A_{i,j}} \right)$.

Figure 2. Multiphonon emission rate (W_{NR} , sec^{-1}) as a function of temperature (K) for $\text{Er}^{3+}: 2\text{H}_{9/2} \rightarrow 4\text{F}_{3/2}$ transition in LaF_3 , which is calculated from the models of Reisfeld [Eq. (10)], Riseberg [Eq. (11)], and Fong [Eq. (14)], respectively.

Figure 3. Temperature (K) dependence of multiphonon emission rate (W_{NR} , sec^{-1}) for $\text{Er}^{3+}: {}^2\text{H}_{9/2} \rightarrow {}^4\text{F}_{3/2}$ transition in LaF_3 host calculated by the Riseberg-model.

Figure 4.

Dependence of multiphonon emission rate (W_{NR} , sec^{-1}) on temperature (K) in terms of (a): the Reisfeld-model of energy gap law (red dash line) and the Fong-model of penta-phonon theory (black solid line), and (b): the Fong-model (black solid line) and the unified model of energy gap law with the addition of $\nu = +2$ quanta (green dot line).

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TABLE 1

Numerical values of effective parameters for multiphonon relaxation rates of RE³⁺ (RE= Nd, Dy and Er) doped halides (LaF₃ and LaCl₃)

Transition	$L_m E_m^2$	$L_m C_{aa} ^2$ (ergs ²) [†]	$\hbar\omega_{max}$ (cm ⁻¹) [‡]	Phonon energy cutoff (cm ⁻¹)	Sum of squares
LaCl ₃ :Nd ³⁺	0.1509	2.1×10^{-33}	259	260	3.37
LaCl ₃ :Dy ³⁺	0.1501	4.2×10^{-32}	231	260	2.16
LaF ₃ :Er ³⁺	0.1400	5.3×10^{-29}	353	360	0.226

[†] NB : $L_m |C_{aa}|^2$ is not a constant for a given host. Therefore, we will need to calculate a specific value for each electronic transition with differing E .

[‡] In multiphonon transitions, the maximum energy phonon mode contributes most significantly to the relaxation processes. Contributions from the lower energy modes do tend to yield effective phonon energy somewhat lower than the cut-off energy typically invoked in mediating the decay.

TABLE 2

Comparison of nonradiative relaxation parameters for various crystals

Hosts	B (sec ⁻¹)	α(cm)	ħω _{max} (cm ⁻¹)	E (cm ⁻¹)	W _{NR} (sec ⁻¹) [‡]
SiO ₂	1.4 × 10 ¹²	3.8 × 10 ⁻³	1100	~2900	2.32 × 10 ⁷ ‡
YAlO ₃	6.425 × 10 ⁹	4.69 × 10 ⁻³	600 cm ⁻¹	2231	53.8 × 10 ³
Y ₂ O ₃	1.204 × 10 ⁸	3.53 × 10 ⁻³	600 cm ⁻¹	~ 2230	56.9 × 10 ³
Y ₃ Al ₅ O ₁₂	2.235 × 10 ⁸	3.50 × 10 ⁻³	700 cm ⁻¹	2227	34.4 × 10 ³
LaF ₃	3.966 × 10 ⁹	6.45 × 10 ⁻³	350 cm ⁻¹	2545	1.32 × 10 ³
LaCl ₃	3.008 × 10 ¹⁰	1.37 × 10 ⁻²	260 cm ⁻¹	2929	5.11 × 10 ⁻⁶
LaBr ₃	1.03 × 10 ¹⁰	1.88 × 10 ⁻²	175 cm ⁻¹	2960	1.00 × 10 ⁻¹⁰

[‡]NR rates calculated at room temperature for the ¹G₄ → ³H₅ transition of Pr³⁺ in a variety of hosts. E corresponds to the energy difference between the lower ¹G₄ and upper ³F₄ Stark levels for each host and was calculated from data tabulated by Kaminskii.³⁵ The multiphonon B and α coefficients are from Reisfeld and Jørgensen¹⁶ with the exception of LaBr₃ being from Wright, et al.¹⁷

^{*}Multiphonon relaxation dominates over the radiative de-excitation such that no 1.3 μm (¹G₄ → ³H₅) luminescence is observed in SiO₂.

TABLE 3

Spontaneous emission probabilities, multiphonon relaxation rates and theoretical QE of Pr^{3+} : $^1\text{G}_4$ state in the lanthanum halides

Host	Spontaneous emission rate (sec^{-1})	Multiphonon relaxation rate (sec^{-1})	Theoretical QE (%)
LaF_3	321.15	1.323×10^3	20
LaCl_3	682.03	5.11×10^{-6}	100
LaBr_3	---	1.00×10^{-10}	100