

Theoretical studies of nonradiative 4f–4f multiphonon transitions in dielectric crystals containing rare earth ions

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Abstract

Detailed calculations have been performed of multiphonon relaxation rates of optical excitations in Nd-doped LiYF₄ and Pr-doped CsCdBr₃ crystals in the frameworks of the exchange charge model of the crystal fields and rigid ion harmonic models of lattice dynamics. It is shown that the empirical energy gap law emerges from the exponential diminishing of spectral densities of n -phonon correlation functions with the increase of an order n . Calculated transition probabilities for 2-, 3-phonon processes agree with experimental data. However, for energy gaps exceeding the maximum phonon energy more than twice, the existing theory which neglects the lattice anharmonicity brings about underestimated relaxation rates.

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1. Introduction

Nonradiative decay rates between crystal field energy levels belonging to different manifolds of rare earth (RE) ions are predominantly determined by the energy gap and the particular host crystal lattice. To describe the experimental data, the energy gap law for the probabilities of nonradiative transitions at low temperatures was introduced [1,2]

$$W = (1/\tau_0) \exp(-a\Delta E/\hbar\omega_M), \quad (1)$$

where a and τ_0 are empirically fitted parameters, ω_M is the highest phonon frequency of the host medium, and ΔE is the energy gap between the populated state and the next lower lying energy level of a RE ion (usually this gap is considered as the difference between energies of the lowest crystal field state of the upper multiplet and the highest crystal field state of the lower multiplet). The minimum number of phonons n needed to bridge the gap

($\Delta E = \hbar[(n-1)\omega_M + \Omega]$), $0 < \Omega < \omega_M$) denotes the order of the process. The theoretical derivation of the energy gap law in the framework of linear mechanism of the electron–phonon interaction [3] based on the substitution of an exponent e^{-an} for $1/n!$ (where n is the number of phonons emitted by the ion) is not satisfactory. Pukhov and Sakun worked out the microscopic model of nonradiative multiphonon transitions using terms of n th order in the Hamiltonian of electron–phonon interaction to calculate the probability of a process that involved n phonons [4]. We consider here this nonlinear mechanism of nonradiative transitions in the framework of a cluster model taking into account interactions between the RE ion and a finite number of its ligands in the first coordination shell. Making use of this model allows calculations of multiphonon transition probabilities without introducing any additional fitting parameters except those involved in the description of the crystal field interaction. The main goal of the present work is to check whether the existing theory is able to predict reliable estimations of multiphonon relaxation rates of impurity RE ions in dielectric crystals.

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2. Probabilities of multiphonon transitions

The Hamiltonian of a RE ion (with the ground electronic configuration $4f^N$) in the lattice site 0, interacting with ligands in sites s , is the sum of the Hamiltonian of a free ion H_{fi} , the crystal field interaction H_{CF} , and the Hamiltonian of the electron–phonon interaction H_{el-ph} ,

$$H_{CF} = \sum_{pk} \sum_s \sum_{i=1}^N B_p^k(s) C_p^k(i), \quad (2)$$

$$H_{el-ph} = \sum_{pk} \sum_{i=1}^N \left[\sum_{s,\alpha} B_{p,\alpha}^k(s) u_\alpha(s, 0) + \frac{1}{2} \sum_{s,\alpha\beta} B_{p,\alpha\beta}^k(s) u_\alpha(s, 0) u_\beta(s, 0) + \dots \right] C_p^k(i). \quad (3)$$

The series (3) is written under the assumption that dynamic displacements of ions from their equilibrium positions in the crystal lattice $\mathbf{u}(s)$ are much smaller than distances between ions. Here C_p^k are the spherical tensor operators, $B_p^k = \sum_s B_p^k(s)$ are the crystal field parameters, $\mathbf{u}(s, 0) = \mathbf{u}(s) - \mathbf{u}(0)$. The dynamic ion displacements can be expanded in terms of the phonon annihilation and creation operators. Constants of the electron–phonon interaction $B_{p\alpha\beta\gamma\dots}^k(s)$ are the derivatives of the crystal field parameters in respect to ligand coordinates $X_{s\alpha}$. The number of independent coupling constants $B_{p\alpha\beta\dots\gamma}^k(s)$, which differ at least by one among n coordinate indices, equals $Z_n = (n+1)(n+2)/2$ for each ligand s (in particular, there are six independent second-order coupling constants which correspond to the set of indices xx, yy, zz, xy, xz, yz).

At zero temperature, a probability of the n -phonon transition between the electronic states i and f with the energy gap $\varepsilon_i - \varepsilon_f = \hbar\omega_0$ can be derived as follows (the n th order term in the expansion (3) is considered as the time dependent perturbation, and the symmetry of the coupling constants $B_{p\alpha\beta\dots\gamma}^k(s)$ under the permutations of the indices $\alpha, \beta, \dots, \gamma$ is taken into account)

$$W_{if}^{(n)} = \frac{2}{\hbar} \left(\frac{\hbar}{\pi} \right)^{n-1} \mathbf{V}_{if} \mathbf{J}_n(\omega_0) \mathbf{V}_{if}^+, \quad (4)$$

where the row vector \mathbf{V}_{if} has elements

$$V_{if,\alpha\beta\dots\gamma}(s) = \sum_{p,k} \langle f | C_p^k | i \rangle B_{p,\alpha\beta\dots\gamma}^k(s), \quad (5)$$

and elements of the matrix $\mathbf{J}_n(\omega_0)$ of multiphonon correlation functions are determined as

$$J_{n,ab}(ss'|\omega_0) = \sum_p J_{n,\alpha\beta\dots\gamma}^{j\mu\dots\nu}(ss'|\omega_0) = \int \dots \int d\omega_1 \dots d\omega_n \delta\left(\omega_0 - \sum_{i=1}^n \omega_i\right) S_{n,ab}(ss'|\omega_1, \omega_2, \dots, \omega_n), \quad (6)$$

$$S_{n,ab}(ss'|\omega_1, \omega_2, \dots, \omega_n) = \frac{1}{n!} \sum_p g_{\alpha i}(ss'|\omega_1) \dots g_{\gamma\nu}(ss'|\omega_n),$$

(the sum is over permutations between different $\alpha\beta\dots\gamma, \lambda\mu\dots\nu$) with the dimensions of $Z_n L \times Z_n L$, where L is the number of ligands, functions $g_{\alpha\beta}(ss'|\omega) = \text{Im} G'_{\alpha\beta}(ss'|\omega)$ are the spectral densities of the lattice Green's functions for differences between displacements of ligands and the RE ion

$$G'_{\alpha\beta}(ss'|\omega) = G_{\alpha\beta}(ss'|\omega) - G_{\alpha\beta}(s0|\omega) - G_{\alpha\beta}(0s'|\omega) + G_{\alpha\beta}(00|\omega), \quad (7)$$

$$G_{\alpha\beta}(ss'|\omega) = \frac{1}{N\sqrt{m_s m_{s'}}} \sum_{jq} \frac{e_\alpha(\mathbf{q}j|s) e_\beta(\mathbf{q}j|s')^*}{\omega^2 - \omega_j(\mathbf{q})^2} \times \exp[i\mathbf{q}(\mathbf{R}_s - \mathbf{R}_{s'})]. \quad (8)$$

Here N is the number of unit cells in a lattice, m_s is the ion mass, \mathbf{R}_s is the lattice vector, $\mathbf{e}(\mathbf{q}j|s)$ is the polarization vector, and $\omega_j(\mathbf{q})$ is the frequency of a phonon with the wave vector \mathbf{q} from the j th branch of the vibration spectrum.

In the framework of linear theory, the transition rate of the n -phonon process equals

$$W_{if}^{(n)} = \frac{2}{\hbar^n} \left(\frac{1}{\pi} \right)^{n-1} \frac{1}{(n-1)!} \exp(-S_{if}) \times \sum_{\alpha\beta s s' p k p' k'} \int d\omega_1 \dots d\omega_n \delta\left(\omega - \sum_1^n \omega_k\right) \times \frac{A_{if}(\omega_1) \dots A_{if}(\omega_{n-1})}{\omega_1^2 \dots \omega_{n-1}^2} \times B_{p\alpha}^k(s) \langle f | C_p^k | i \rangle g_{\alpha\beta}(ss'|\omega_n) \langle i | C_{p'}^{k'} | f \rangle B_{p'\beta}^{k'}(s') \quad (9)$$

where

$$A_{if}(\omega) = \sum_{\substack{\alpha\beta s s' \\ p k p' k'}} B_{p\alpha}^k(s) (\langle i | C_p^k | i \rangle - \langle f | C_p^k | f \rangle) g_{\alpha\beta}(ss'|\omega) \times (\langle i | C_{p'}^{k'} | i \rangle - \langle f | C_{p'}^{k'} | f \rangle) B_{p'\beta}^{k'}(s') \quad (10)$$

and

$$S_{if} = \frac{1}{\pi\hbar} \int A_{if}(\omega) d\omega / \omega^2 \quad (11)$$

is the Huang-Rhys parameter. The expression (9) includes the multiple ($n-1$ times) product of the one-phonon spectral densities projected on the adiabatic lattice deformations (promoting phonons) and the only one factor corresponding to the nonadiabatic deformation (an accepting phonon). The transition rate may be approximated by the following:

$$W_{if}^{(n)} \cong W_{if}^{(1)} e^{-S_{if}} S_{if}^{n-1} / (n-1)!, \quad (12)$$

the first factor at the right hand side stands for the virtual one-phonon transition probability at the average phonon frequency. In the case of intraconfiguration f–f transitions, the interaction with the adiabatic deformations is extremely weak, and the real nonradiative transition rates are greatly underestimated by the expression (9).

3. Electron–phonon coupling constants

To calculate the electron–phonon coupling constants, we need to know the explicit dependence of the crystal field parameters on ligand coordinates. In the framework of the exchange charge model [5,6], a contribution to the crystal field from each ligand is presented by the following expression

$$B_p^k(s) = e^2 \left[-q_s(1 - \sigma_p) \langle r^p \rangle + \frac{2(2p+1)}{7} R_s^p S_p(R_s) \right] (-1)^k C_p^{-k}(\vartheta_s, \varphi_s) / R_s^{p+1}, \quad (13)$$

where eq_s is the ligand charge, and R_s, θ_s, φ_s are its spherical coordinates, $\langle r^p \rangle$ are moments of the 4f electron radial wave function, and σ_p are the shielding constants [7] accounting for the linear screening of 4f-electrons by outer $5s^2, 5p^6$ -electron shells. Corrections to the Coulomb interaction due to the spatial distribution of the electron density of the nearest neighbor ions with the outer filled $n''s^2$ and $n''p^6$ electron shells are described as the field of exchange charges proportional to the quadratic forms of the overlap integrals:

$$S_p = G_s |S_s|^2 + G_\sigma |S_\sigma|^2 + \gamma_p G_\pi |S_\pi|^2, \quad (14)$$

$$S_s = \langle 430 | n''00 \rangle, \quad S_\sigma = \langle 430 | n''10 \rangle,$$

$$S_\pi = \langle 43 \pm 1 | n''1 \pm 1 \rangle,$$

the kets $|nlm\rangle$ are specified by the standard principal, orbital and magnetic quantum numbers, $\gamma_2 = 3/2$, $\gamma_4 = 1/3$, $\gamma_6 = -3/2$. Dependences of the overlap integrals on a distance R between the RE ion and the ligand can be computed by making use of radial wave functions of RE [8] and ligand [9] ions. Dimensionless parameters of the model G_s, G_σ, G_π are obtained from a comparison of the calculated and measured crystal field energies.

4. Multiphonon correlation functions

If the spectral densities of the lattice Green's functions $J_{1,\alpha}^i(ss'|\omega) = g_{\alpha i}(ss'|\omega)$ are known, the spectral densities of multiphonon correlation functions (6) can be computed using the recurrent relations [10]:

$$J_{n,\alpha\beta\cdots\gamma}^{\lambda\mu\cdots\nu}(ss'|\omega_0) = \frac{1}{n} \int_a^b d\omega J_{1,\alpha}^{\lambda}(ss'|\omega) J_{n-1,\beta\cdots\gamma}^{\mu\cdots\nu}(ss'|\omega_0 - \omega), \quad (15)$$

where $a = 0$ for $\omega_0 < (n-1)\omega_M$, and $a = \omega_0 - (n-1)\omega_M$ for $(n-1)\omega_M < \omega_0 < n\omega_M$; $b = \omega_M$ for $\omega_0 > \omega_M$, and $b = \omega_0$ for $\omega_0 < \omega_M$. For large n , the spectral densities of multiphonon correlation functions can be approximated by Gaussians with the following scaling properties:

$$J_{n-1}(\omega, \omega_{n-1}, \Delta_{n-1}^2) = \frac{A}{(\pi\Delta_{n-1}^2/2)^{1/2}} \times \exp \left[-2(\omega - \omega_{n-1})^2 / \Delta_{n-1}^2 \right],$$

$$J_n(\omega, \omega_n, \Delta_n^2) = J_{n-1}(\omega, \omega_{n-1}/k, \Delta_{n-1}^2/k), \quad k = \frac{n-1}{n}.$$

The transition probability (4) contains a number of terms (for example, in a case of the 4-phonon process, for a RE ion interacting with eight ligands, we have to calculate 120^2 convolutions (6)). However, the problem can be simplified. Each term in the Hamiltonian (3) contains relative displacements of the fixed ligand and the RE ion. Correspondingly, in the framework of the first order perturbation theory, the transition probability contains only products of the positive spectral densities of diagonal autocorrelation functions $g_{\alpha\alpha}(ss'|\omega)$ or products of spectral densities of non-diagonal correlation functions with alternating signs that satisfy the inequality $g_{\alpha\beta}(ss'|\omega) < g_{\alpha\alpha}(ss'|\omega)$. Thus, it is possible, at least in the case of a large order n of a relaxation process, to neglect non-diagonal (in respect to ligand labels) elements of the matrix $J_{n,ab}(ss'|\omega)$. The next simplifying step may be done by neglecting non-diagonal elements in the blocks $J_{n,ab}(ss'|\omega)$. We restrict our attention to the spontaneous multiphonon relaxation. In this case we can approximate the transition probability by the multiplicative expression

$$W_{if}^{(n)} = \frac{2\pi}{\hbar^2} \langle \mathbf{V}_{if}^{(n)2} \rangle_{Av} Sp \left[\left(\frac{\hbar}{\pi} \right)^n \mathbf{J}_n(\omega_0) \right], \quad (16)$$

where the mean square value of coupling constants is defined through the scalar product

$$\mathbf{V}_{if} \cdot \mathbf{V}_{if}^+ = Z_n L \langle \mathbf{V}_{if}^{(n)2} \rangle_{Av}. \quad (17)$$

The semi-logarithmic plots of gap dependences of dimensionless traces $Sp[\alpha_n \mathbf{J}_n(\omega)]$ (where $\alpha_n = \sec^{-1} \cdot [\hbar / (\pi \text{\AA}^2)]^n$) calculated for two crystal lattices are presented in Fig. 1 (for details see the next section). The gap dependence of the sums of these traces may be well approximated by the direct line approximating a common tangent to individual traces, and the dependence of the lattice factor in (16) on the energy gap ω_0 can be presented by a single exponential function for the fixed crystal.

As it follows from simple physical arguments, and has been confirmed by our calculations, the averaged squares of coupling constants increase with the order n of a process (at least, by an order of magnitude with n increased by unity). This increase of the electronic factor (the calculated dimensionless ratios $\text{\AA}^2 \langle (\mathbf{V}_{if}^{(n+1)})^2 \rangle_{Av} / \langle (\mathbf{V}_{if}^{(n)})^2 \rangle_{Av}$ are close to 10^2) compensates partly for a strong dependence of the lattice factor on the gap, but the exponential diminishing of the transition rate survives.

5. Simulations of the nonradiative transition rates in $\text{LiYF}_4:\text{Nd}^{3+}$ and $\text{CsCdBr}_3:\text{Pr}^{3+}$

In this section, we present examples of calculations of multiphonon relaxation rates for RE ions in ionic crystals. The LiYF_4 activated by Nd^{3+} , and the Pr-doped CsCdBr_3 are selected as model objects because experimental data on relaxation rates in these crystals are available, and the

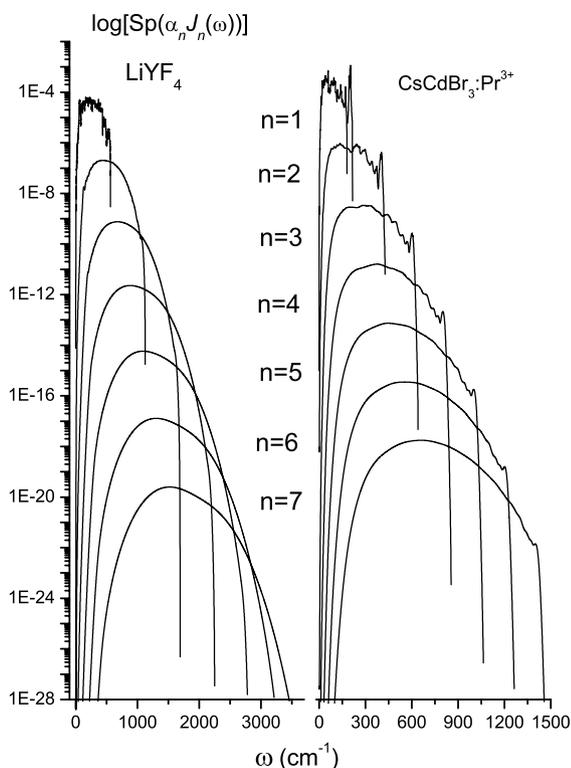


Fig. 1. Traces of multiphonon correlation functions vs the gap frequency.

crystal field effects and the vibration spectra of the crystal lattices have been investigated earlier.

LiYF₄ crystals belong to the C_{4h}^6 space group. RE³⁺ ions substitute for Y³⁺ ions in sites with the S_4 point symmetry (the nearest surroundings includes eight fluorine ions). The vibration spectrum of the LiYF₄ crystal lattice was studied in [11]. Results of optical and neutron inelastic scattering experiments were described successfully in the framework of the rigid-ion model. Using parameters of this model, we computed frequencies and polarization vectors of vibrations for 32,000 wave vectors distributed uniformly over the irreducible part of the Brillouin zone. Thus the database corresponding to $36 \times 256,000$ normal modes of the lattice was obtained. Imaginary parts of the lattice Green's functions (8) were calculated at the equally spaced 1120 points $\omega_f (0 \leq \omega_f \leq \omega_M)$ on the frequency axis by numerical integration over the Brillouin zone. The matrices of multiphonon spectral densities $J_n(\omega)$ in the space of relative displacements of ions within the complex containing the Y³⁺ ion and its eight ligands for $n = 2-7$ with dimensions of $4(n+1)(n+2)$ were simulated as functions of a discrete variable $\omega = \omega_f (f = 1:1120)$. The traces of spectral densities $Sp[\alpha_n J_n(\omega)]$ (see Fig. 1) have maximum values at the frequencies $\omega = n\omega_{eff}$, and the frequency $\omega_{eff} = 225 \text{ cm}^{-1}$ can be considered as the frequency of the most effective lattice vibration; it should be noted that ω_{eff} is much smaller than the maximum phonon frequency $\omega_M = 560 \text{ cm}^{-1}$. The curves $Sp[\alpha_n J_n(\omega)]$ and $Sp[\alpha_{n+1} J_{n+1}(\omega)]$ intersect at the points $\omega_{n,n+1}$ that equal 1030 cm^{-1} ($n = 2$), 1480 cm^{-1} ($n = 3$), 1930 cm^{-1} ($n = 4$), and 2380 cm^{-1} ($n = 5$). Begin-

ning from the value of the energy gap $\hbar\omega_0 > \hbar\omega_{n,n+1}$, the contribution of the $(n+1)$ -phonon process definitely dominates in the corresponding nonradiative transition. Such a process becomes the most effective one at the gap value essentially less than $n\omega_M$.

To obtain the transition probabilities, matrix elements of the Hamiltonian (3) were calculated with the eigenfunctions of the Hamiltonian $H_{fi} + H_{CF}$ defined in the total space of $364|4f^n \gamma LS J J_z\rangle$ -states of Nd³⁺ ($4f^3$), the crystal field parameters and the measured crystal field energies from Ref. [12] were used (see Fig. 2). Parameters of the exchange charge model were determined from the crystal field splittings. The interaction of the localized 4f-electrons with the nearest neighbors of the RE ion is responsible for the major contributions to the crystal field parameters. By taking into account interactions of the RE ion with its nearest neighbors only, we can avoid calculations of infinite number of the lattice correlation functions. This greatly simplifying approach is used in what follows. Results of calculations of probabilities of spontaneous 2-, 3-, 4- and 5-phonon transitions between the crystal field sublevels and the total relaxation rates that may be compared with the measured lifetime of the corresponding upper sublevel are presented in Table 1. Because experimental data available from literature were taken mainly at the nitrogen temperature, the relaxation rates were calculated not only for the lowest sublevel of the upper multiplet, but also for some excited sublevels that might be populated.

A comparison of calculated and measured relaxation rates shows that there is a good agreement only for small enough energy gaps ($\omega_0 \leq 2\omega_M$) when it is necessary to

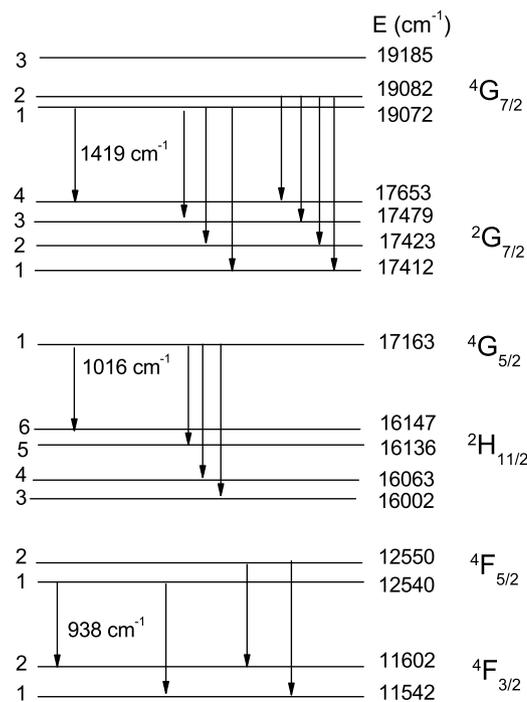


Fig. 2. Energy levels of Nd³⁺ in LiYF₄ and paths of nonradiative transitions.

Table 1
Calculated and measured probabilities $W^{(n)}$ (s^{-1}) of n -phonon transitions in $\text{LiYF}_4:\text{Nd}^{3+}$

Path	Gap (cm^{-1})	$W^{(2)}$	$W^{(3)}$	$W^{(4)}$	$W^{(5)}$	Total rate $T = 0$ K	Exper. $T = 77$ K
${}^4G_{7/2}(1) \rightarrow {}^2G_{7/2}(4)$	1419	–	1.67×10^6	5.50×10^6	0.38×10^6	8.3×10^6	8.3×10^7
$\rightarrow {}^2G_{7/2}(3)$	1593	–	0.01×10^6	0.47×10^6	0.10×10^6		[13,14]
$\rightarrow {}^2G_{7/2}(2)$	1649	–	–	0.11×10^6	0.05×10^6		
${}^4G_{7/2}(2) \rightarrow {}^2G_{7/2}(4)$	1429	–	0.58×10^6	2.18×10^6	0.17×10^6	2.9×10^6	
${}^4G_{5/2}(1) \rightarrow {}^2H_{11/2}(6)$	1016	0.58×10^7	8.41×10^7	0.62×10^7	0.08×10^6	1.71×10^8	2.22×10^8
$\rightarrow {}^2H_{11/2}(5)$	1027	0.67×10^7	3.93×10^7	0.17×10^7	0.05×10^6		[15]
$\rightarrow {}^2H_{11/2}(4)$	1100	–	2.39×10^7	0.32×10^7	0.08×10^6		
${}^4F_{5/2}(1) \rightarrow {}^4F_{3/2}(2)$	938	4.28×10^8	2.89×10^8	0.05×10^8	–	1.07×10^9	4.5×10^9
$\rightarrow {}^4F_{3/2}(1)$	998	0.74×10^8	2.68×10^8	0.08×10^8	–		[16]
${}^4F_{5/2}(2) \rightarrow {}^4F_{3/2}(2)$	948	3.20×10^8	2.42×10^8	0.04×10^8	–	0.81×10^9	
$\rightarrow {}^4F_{3/2}(1)$	1008	0.38×10^8	2.00×10^8	0.03×10^8	–		

consider processes that involve no more than three phonons. On no account can the order of the most effective process be estimated from the ratio between the gap and the maximum phonon frequency. In particular, in the case of ${}^4G_{5/2} \rightarrow {}^2H_{11/2}$ nonradiative transition ($\omega_0 \leq 1.9 \omega_M$), the two-phonon processes are allowed, but the corresponding probability is about an order of magnitude less than the probability of the three-phonon transition. Similarly, in the case of nonradiative relaxation of the ${}^4G_{7/2}$ multiplet ($\omega_0 \geq 2.5 \omega_M$), three-phonon transitions to the crystal field states of the nearest ${}^2G_{7/2}$ multiplet are allowed, but the probabilities of these processes are less than probabilities of the four-phonon transitions.

The calculated values of the transition rates as compared with the measured lifetimes of the excited states are underestimated up to two orders of magnitude if the gap exceeds $3 \omega_M$. The disagreement is too large to be related to possible errors in estimations of coupling constants. The excited state lifetimes usually shorten with temperature due to increase of the relaxation rates. The temperature dependence of the n -phonon transition probability may be approximated by the factor $(1 - e^{-h\omega_{\text{eff}}/kT})^{-n}$ that does not differ too much from unity for $T < 100$ K. From similar calculations of probabilities of 3-, 4- and 5-phonon ${}^3P_1 - {}^3P_0$ transitions ($\omega_0 = 571 \text{ cm}^{-1}$) in the impurity symmetrical $\text{Pr}^{3+}\text{-Cd}^{2+}$ vacancy -Pr^{3+} pair centers in CsCdBr_3 which substitute for three adjacent Cd^{2+} ions ($\omega_M = 180 \text{ cm}^{-1}$, frequencies of local modes equal $197\text{--}204 \text{ cm}^{-1}$ [17]), we obtained also strongly underestimated (about 60 times less) relaxation rates for the 3P_1 states as compared with the experimental data [18].

Contributions due to the n th order terms in the electron–phonon interaction prevail in the n -phonon transition rate, but the total contribution of all lower order terms may play a comparable role. In particular, the 4-phonon process can be realized through two-step (2 + 2)- or (1 + 3)-processes. Calculations of the probability of the 4-phonon transition ${}^4F_{5/2} \rightarrow {}^4F_{7/2}$ at the gap of 1584 cm^{-1} in $\text{LiYF}_4:\text{Er}^{3+}$ have shown (the sum over intermediate ion states included only sublevels of the multiplets involved into the transition) that the positive second order terms of the type (1 + 3)·(1 + 3) and the negative cross terms (4)·(1 + 3)

diminish the first order term (the total contribution of the second order terms is approximately -10% of the main term). In this case the calculated contribution into the relaxation rate caused by the linear mechanism of nonradiative transitions is about three orders of magnitude less than the measured rate.

6. Conclusions

Probabilities of nonradiative multiphonon spontaneous transitions between crystal field sublevels of different $4f^N$ – multiplets of impurity Nd^{3+} ions in LiYF_4 and Pr^{3+} ions in CsCdBr_3 have been calculated using realistic models of the vibration spectrum of the host crystal lattice. The local lattice deformation and changes of the vibration spectrum due to a perturbation of the CsCdBr_3 lattice by an impurity Pr^{3+} -dimer were taken into account. Both linear and non-linear mechanisms of multiphonon relaxation of optical excitations were considered. The presented approach differs from preceding investigations because of avoiding any procedure of averaging over the multiplet states (probabilities of the transitions between the crystal field states are considered), and because the computed phonon spectral densities are used to describe dynamic properties of the real crystal lattices. The Hamiltonian of the electron–phonon interaction contained all terms from the first up to the 5th order in differences between displacements of an impurity RE ion and its nearest neighbors with the coupling constants calculated in the framework of the exchange charge model.

From calculations of probabilities of transitions which involve up to five phonons, it follows that the nonlinear mechanism of nonradiative transitions between crystal field sublevels divided by gaps exceeding more than twice the maximum phonon frequency is much more effective than the linear one. The linear mechanism of multiphonon relaxation is not effective due to very small values (<0.1) of Huang-Rhys parameters for transitions between the crystal field $4f^N$ states of RE ions. The minimum number n of emitted phonons does not determine the order of the most effective relaxation path. Results of calculations show unambiguously that $(n + 1)$ -phonon processes can be much more effective than transitions involving n phonons due to

a larger volume in the frequency space which contributes to the corresponding convolutions of phonon spectral densities. The empirical energy gap law emerges from the specific gap dependences of multiphonon correlation functions.

The calculated transition rates are underestimated up to one-two orders of magnitude if the gap between the lowest sublevel of the upper multiplet and the highest sublevel of the lower multiplet exceeds more than twice the maximum phonon frequency. The task of reliable estimating the n -phonon relaxation rate for $n \geq 3$ remains a challenging theoretical problem. The harmonic approximation is likely to be invalid when the lattice excitation involves creation of more than three phonons, however, so far no detailed study of lattice anharmonicity effects in the theory of multiphonon relaxation has been carried out.

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