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Multiple-phonon nonradiative relaxation: Experimental rates in fluoride crystals doped with Er^{3+} and Nd^{3+} ions and a theoretical model

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The multiphonon relaxation (MR) rates for a large number of 3- to 5-phonon transitions of Er^{3+} ions in $LiYF_4$ and LaF_3 crystals were measured at 77 K. The MR rates of Nd^{3+} and Er^{3+} ions in these crystals have been analyzed with a point-charge (or ionic) nonlinear relaxation mechanism and a covalent nonlinear relaxation mechanism, rather than the traditional linear relaxation mechanism. The functional dependencies of the experimental MR rates on the number of phonons n participating in the radiationless transitions were explained in terms of the two nonlinear coupling mechanisms. The mean values of the parameter of the theory $\eta = u^2/R_0^2$, where R_0 is the equilibrium minimal distance between the rare-earth ion and the ligands and u is the amplitude of the vibrations of the ligands, have been evaluated in these crystals for $n = 3$–4 where the contribution of the exchange interaction is small. On the basis of these calculations it was established that the strength of dynamic electron-phonon coupling is larger in LaF_3 than in $LiYF_4$. Also, the influence on the MR rates of the exchange interaction between the $4f$ electron and the ligands has been analyzed. Its inclusion gives higher theoretical MR probabilities and better agreement with the experimental relaxation rates.

I. INTRODUCTION

During the past thirty years the investigation of multiphonon relaxation (MR) in laser crystals doped with the rare-earth (RE) ions has been an active field of research in fundamental solid state physics. Systematic experimental studies of MR were started in Refs. 1–4, where the MR rates $[W_{MR}(n)]$ of excited electronic states were measured in various crystals doped with Nd^{3+}, Dy^{3+}, Ho^{3+}, and Er^{3+} ions. The dependencies of $W_{MR}(n)$ on the energy gap $(\Delta E_{\min})$ to the next multiplet below, the number of phonons n participating in the radiationless transition, and the temperature were analyzed. Also, the empirical theoretical dependence of MR probability versus $\Delta E_{\min}$ known as the energy-gap law: $W(\Delta E, T=0\ \mathrm{K}) = W_0 \exp(-\alpha \Delta E_{\min})$, where W_0 and α are experimentally determined parameters, was proposed. As a first approximation this law provided an accurate description of the experimental dependencies of MR probabilities on $\Delta E_{\min}$ in different crystals. A detailed review of these experimental measurements can be found elsewhere.[5] These results showed the energy-gap law was accurate to about 1–2 orders of magnitude. However, the time resolution and sensitivity of the early experimental apparatus did not allow measurements of the rates for radiationless transitions involving 4 or fewer phonons. The indirect methods used to determine these rates gave several orders of magnitude spread in the measured MR data and therefore, cast some doubt on the confidence of these measurements. A considerable improvement in experimental accuracy was achieved in the results of Ref. 6. Here direct laser excitation and direct measurement using time correlated photon-counting techniques gave subnanosecond time resolution to the kinetics of the fluorescence decay. The application of this method allowed investigations of MR processes in a wide number of fluoride and oxide crystals doped with Nd^{3+} ions.[7,8] The MR probability versus energy gap $\Delta E_{\min}$ in $Y_3Al_5O_{12}$ (YAG), $YAlO_3$ (YAP), $Gd_3Ga_5O_{12}$ (GGG), $CaMoO_4$, LaF_3, and YLF crystals doped with Nd^{3+} ions[8] showed an increase in the slope for $\Delta E_{\min} \leq 2000\ \mathrm{cm}^{-1}$ when compared to other measurements for $\Delta E_{\min} > 2000\ \mathrm{cm}^{-1}$ in YAG, YAP, GGG, and LaF_3 doped with Er^{3+} and Ho^{3+} ions.[4,9] Thus it appears that the MR rates for transitions involving a larger number of phonons are enhanced above those expected from the predictions of a single slope energy-gap law.

Along with the experiments, the theoretical investigations of MR processes have steadily advanced and detailed reviews can be found elsewhere.[5,9–12] The linear theory of Miyakawa and Dexter[13] predicts an exponential energy-gap law but is only valid for strong and intermediate electron-phonon coupling. A modified exponential energy-gap law reconciles the large variation in the preexponential factor for transitions involving only a few phonons.[14] The nonlinear theory of Pukhov and Sakun[15] is valid for weak electron-phonon coupling and has the advantage of expressing the MR rates in terms of the reduced matrix elements $\langle J' \| U^{(k)} \| J \rangle$ familiar from Judd-

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Ofelt theory. However, neither theory adequately copes with the enhanced MR rates observed for transitions involving a large number of phonons ($n > 3$). It is well known from quantum mechanics that a short-range exchange interaction dealing with the overlap of wave functions is possible between the RE ion and the ligands. For most RE-doped crystals it is necessary to consider this interaction in the calculation of the nonradiative transition rates. It is expected to have most influence for transitions with large n where the perturbation potential arising from the ligands shifts to the ligand itself.

The aim of this work is to use new and old measurements of the MR rates in LaF_3 and $LiYF_4$ crystals doped with Er^{3+} and Nd^{3+} ions in a comparison with all aspects of the theory in order to explain the $W_{MR}(n)$ dependencies in these crystals.

II. THEORY

The main physical mechanisms contributing to MR in systems with weak electron-phonon coupling are summarized here to show their principal differences. The Hamiltonian for a RE impurity center in a crystal can be written as

$$H = \overline{H}_e + \overline{H}_l + \overline{V}_{cr} \tag{1}$$

where $\overline{H}_e$, $\overline{H}_l$, and $\overline{V}_{cr}$ are the Hamiltonians for the optically active electron, crystal lattice, and the electron-lattice interaction, respectively. The electron-lattice interaction $\overline{V}_{cr}$ depends on the distance between the impurity ion and the ligands. Assuming a small displacement (u) of the ions of the lattice from their equilibrium positions ($r = R_0$) it is possible to expand $\overline{V}_{cr}$ in a Taylor's series,

$$\begin{aligned} V_{cr}(R_0+u) = V_{cr}(R_0) &+ \left[\frac{\partial V_{cr}}{\partial r}\bigg|_{R_0} \right] u \\ &+ \left[\frac{\partial^2 V_{cr}}{\partial r^2}\bigg|_{R_0} \right] u^2 + \dots \\ &+ \left[\frac{\partial^n V_{cr}}{\partial r^n}\bigg|_{R_0} \right] u^n + \cdots . \end{aligned} \tag{2}$$

The first term in Eq. (2) describes the static crystal field which determines the Stark splitting of the RE ion energy levels. The other terms describe the dynamical part of the crystal field that is responsible for the electron-phonon interaction (EPI) and is the origin of nonradiative relaxation.

Historically, the first theory for MR was based on the differences in the form and position of the adiabatic potential-energy surfaces between the initial and final electronic states. The linear term in Eq. (2), $(\partial V/\partial r|_{R_0})u$, is responsible for the shift of the lattice nuclei from their equilibrium positions (in terms of the adiabatic potentials this is the shift of their minima). The second-order term $(\partial^2 V/\partial r^2|R_0)u^2$ is responsible for the change of the frequencies of the lattice vibrations (the change of the shape of the adiabatic potentials) in the initial and final electronic states. For simplicity the MR rates have been most often calculated using the linear term $(\partial V/\partial r|R_0)u$ in first-order perturbation theory with the matrix elements evaluated over the nondiagonal electronic states. Thus, the second-order term was generally neglected meaning the MR rates were calculated with the only contribution being the shift in the equilibrium positions of the lattice nuclei. This particular theory is often called the linear (or shifted) relaxation mechanism.[5,10]

Miyakawa and Dexter[13] calculated the MR probability with this relaxation mechanism and theoretically derived the exponential energy-gap law. Harmonic lattice vibrations and a single frequency were assumed so that phonons with only one frequency participated in the radiationless transition. The parameter specifying the strength of electron-phonon coupling and defining the shift of the minima of the adiabatic potentials is the Huang-Rhys parameter, S, and is the main parameter of the linear relaxation mechanism. This theory gives the probability of a spontaneous ($T = 0$ K) n phonon radiationless transition in terms of S as

$$W_{MR}(T=0\ \mathrm{K}) = W_0 \exp\left[-n \left[\ln\left[\frac{n}{S} \right] - 1 \right] \right] . \tag{3}$$

Examination of Eq. (3) reveals that in the case of weak electron-phonon coupling, ($S \ll 1$), W_{MR} tends to zero, particularly with an increase in the number of phonons n. Since the data suggest enhanced MR rates for large energy gaps, another relaxation mechanism characterized by all the terms of Eq. (2) could be effective for weak EPI. This idea was developed mathematically in Ref. 15 and later this mechanism was called the ionic or point-charge nonlinear mechanism.[5]

In the nonlinear theory the crystal potential is formed by the Coulomb interaction of the $4f$ electrons with the ligands, which are treated as point charges and the main contribution to the n phonon process is specified by the nth term $(\partial^n V/\partial r^n|R_0)u^n$ of Eq. (2). Again assuming harmonic lattice vibrations and a single frequency and having averaged over the wave functions of all Stark levels of the A and A' multiplets participating in the radiationless transition, the averaged MR probability between two Stark sublevels α and α' of the appropriate multiplets was derived as[15]

$$\begin{aligned} \overline{W}_{\alpha-\alpha'}(T=0\ \mathrm{K}) = {} & \frac{ze^2 e_s^2}{c\bar{\nu}\hbar^2 R_0^2} \\ & \times \sum_{k=2,4,6} \mu_{lk}(AA') \left[\frac{(2n+2k)!}{(2k+1)!n!} \right] \\ & \times (\bar{\xi}^k / R_0^k)^2 \eta^n . \end{aligned} \tag{4}$$

In Eq. (4) R_0 is the radius of the first coordination shell of the impurity ion, z is the coordination number of the ligands, c is the velocity of light, $\bar{\nu}$ is the frequency of phonons participating in the radiationless transition in [cm^{-1}], e is the charge of the $4f$ electron, e_s is the effective charge of the s ligand, $\hbar$ is Planck's constant, and l is the orbital angular momentum of the optical electron (for the $4f$ orbital $l = 3$). Also

$$\mu_{lk}(AA')=(2l+1)^2\frac{1}{(2J+1)(2J'+1)}\begin{bmatrix} l & l & k \\ 0 & 0 & 0 \end{bmatrix}^2 \times\langle 4f[A']J'\|U^{(k)}\|4f[A]J\rangle^2 , \tag{5}$$

where

$$\begin{bmatrix} l & l & k \\ 0 & 0 & 0 \end{bmatrix}$$

is the $3j$ symbol,[16] J' and J are the full momentum of the initial and final states, respectively, and $\langle 4f[A']J'\|U^{(k)}\|4f[A]J\rangle$ is the reduced matrix element of the unit tensor operator of rank k for the transitions within the $4f$ electronic configuration. The same matrix elements are used for the calculation of the radiative spontaneous emission probability between two multiplets A and A' with the Judd-Ofelt theory. Other parameters in Eq. (4) are the following: $\bar{\xi}^k$ is the mean value of the kth power of the radius of the optical electron and $\eta=u^2/R_0^2$ is the empirical parameter of the theory that is determined by experiment and has values in the range of $10^{-3}-10^{-4}$.[5] Using a Stirling approximation,

$$n!\cong(n/e)^n(2\pi n)^{1/n}(1+\cdots) , \tag{6}$$

and it is possible to reduce Eq. (4) to the well-known exponential energy-gap law.

It is convenient to write

$$E_k(n)=\eta^n(\bar{\xi}^k/R_0^k)^2c_k'(n)(2l+1)^2\begin{bmatrix} l & l & k \\ 0 & 0 & 0 \end{bmatrix}^2\frac{ze_s^2}{\bar{\nu}\hbar R_0^2} , \tag{7}$$

where $c_k'(n)=[(2n+2k)!/(2k+1)!n!]$, and consider the $E_k(n)$ as intensity parameters for the n-phonon radiationless transition. These would be similar to the Ω_k parameters for radiative transitions in the Judd-Ofelt theory. Equation (4) then becomes

$$\overline{W}_{\alpha-\alpha'}(T=0\text{ K})=\frac{1}{137}\frac{1}{(2J+1)(2J'+1)}\sum_{k=2,4,6}E_k(n)\langle 4f[A']J'\|U^{(k)}\|4f[A]J\rangle^2 . \tag{8}$$

For large n the perturbation potential arising from the ligand vibrations shifts closer to the ligand itself. Therefore overlapping effects between the $4f$ electron shell and the electronic clouds of the ligands might be significant[17] and it becomes necessary to consider the covalence of the chemical bonding of optical electron and the ligand together with the Coulomb interaction of the point charges. The form of exchange interaction is[18,19]

$$\overline{V}_{\text{ex}}\sim\exp(-2\alpha r) , \tag{19}$$

where the parameter α determines the extent of the overlap between the wave functions of the $4f$ electron and the ligands. Then the full Hamiltonian of the interaction between the $4f$ electron and the lattice may be written as the sum of the point-charge and exchange interactions

$$\overline{V}_{cr}=\overline{V}_{\text{pc}}+\overline{V}_{\text{ex}} . \tag{10}$$

It was shown in Ref. 18 that it was possible to write the averaged probability $\overline{W}_{\alpha-\alpha'}(n)$ of the n phonon radiationless transition between two Stark levels α and α' as the sum of the point-charge nonlinear (W^{pc}) and exchange (covalent) nonlinear (W^{ex}) relaxation mechanisms:

$$\overline{W}_{\alpha-\alpha'}^{\text{tot}}=\overline{W}_{\alpha-\alpha'}^{\text{pc}}+\overline{W}_{\alpha-\alpha'}^{\text{ex}}=\sum_{k=2,4,6}W_k^{\text{pc}}+\sum_{k=2,4,6}W_k^{\text{ex}} . \tag{11}$$

The relative contributions of the exchange-nonlinear and the point-charge nonlinear relaxation mechanisms to the MR probability were determined. It was shown that for the same k, the ratios of the probabilities for the different mechanisms were

$$\overline{W}_k^{\text{ex}}/\overline{W}_k^{\text{pc}}=(B_k^0/a_k^0)^2\beta_k , \tag{12}$$

where

$$a_k^0=\frac{4\pi ee_s\bar{\xi}^k}{(2k+1)R_0^{k+1}} \tag{13}$$

is the point-charge model parameter and

$$B_k^0=8\pi e^2\frac{G_s|S_s|^2+G_\sigma|S_\sigma|^2+G_\pi\gamma_k|S_\pi|^2}{7R_0} \tag{14}$$

is the parameter for the model of the exchange interaction.[19]

The physical sense of Eq. (14) is as follows. The B_k^0 parameter is proportional to the square of the overlap integrals of the $4f$ wave functions with the wave functions of the external electronic shells of the ligands. For the important practical cases (the oxygen and fluorine ions surrounding the RE^{3+} ions) these are p_σ, p_π, and s orbitals. In Eq. (14) $G_\nu(\nu=\sigma,\ \pi,\text{ and } s)$ are the crystal-field fitting parameters. The overlap integrals are defined as

$$S_\nu=S_\nu^0\exp(-\alpha_\nu R_0) , \tag{15}$$

where S_ν^0 is another parameter of the exchange interaction model and γ_k is given by

$$\gamma_k=2-k(k+1)/12 . \tag{16}$$

The β_k function in Eq. (12) depends in a complicated manner on the number of phonons n and $\tau=2\alpha_\nu R_0$. For the simplest case when the overlap involves only a single type of ν orbital the following expression for β_k was obtained:[15]

$$\beta_k=\left[\frac{(2k)!n!2^n}{(2n+2k)!}\right]\tau^{2n}D(n) , \tag{17}$$

where

$$D(n)=\sum_{p=0}^{\mathrm{Int}(n/2)}\left[\frac{(2n-4p+1)}{(2p)!!(2n-2p+1)!!}\right][T_{n-2p}(\tau)]^2 . \tag{18}$$

In Eq. (18) Int$(n/2)$ is the integer part of $n/2$ and

$$T_{n-2p}(\tau)=\sum_{m=0}^{n-2p}\frac{(n-2p+m)!\tau^{-m}}{m!(n-2p-m)!2^m} . \tag{19}$$

Finally, assuming the limit of weak electron-phonon coupling, harmonic lattice vibrations, and a single frequency, the full averaged rate of the n-phonon radiationless transition between any two Stark levels α and α' of A and A' multiplets can be written as the sum of two terms:

$$\overline{W}_{\alpha-\alpha'}(n)=\overline{W}^{\,\mathrm{pc}}(n)+\overline{W}^{\,\mathrm{ex}}(n)=\sum_k W_k^{\mathrm{pc}}\left[1+\frac{W_k^{\mathrm{ex}}(n)}{W_k^{\mathrm{pc}}(n)}\right] . \tag{20}$$

The rates between Stark levels must be combined to yield the full relaxation rate between adjacent multiplets. In a single-mode approximation the full MR probability $W(A-A')$ between two multiplets A and A' is

$$W(A-A')=g\overline{W}_{\alpha-\alpha'}(n) , \tag{21}$$

where g is the number of transitions from the Stark level of multiplet A to the Stark levels of multiplet A' that participate with the minimum number of phonons. The parameter g is calculated as

$$g=\sum_{\alpha} n_\alpha M_\alpha , \tag{22}$$

where n_α is the population of a Stark level of multiplet A (if $T=0$ K, then $n_\alpha=1$) and M_α the number of such transitions.

III. EXPERIMENTAL TECHNIQUE

The $\mathrm{LiYF_4{:}Er^{3+}}$ crystals used in this work were grown by Airtron Corp. in a platinum system under an HF atmosphere. Two crystals were used with $\mathrm{Er^{3+}}$ concentrations of approximately 3% and 0.1% by weight. The $\mathrm{LaF_3{:}Er^{3+}}$ and $\mathrm{LaF_3{:}Nd^{3+}}$ crystals were grown at the Solid State Department of the General Physics Institute (Moscow, Russia) by the Stockbarger method under a fluorine atmosphere. The concentration of $\mathrm{Er^{3+}}$ and $\mathrm{Nd^{3+}}$ ions was 1.2% and $\sim 1\%$, respectively. A tunable dye laser (model DLII, Molectron Corp.) pumped by a nitrogen pulsed laser (model UV14) with a repetition frequency of 13 Hz was used for direct excitation of the $\mathrm{Er^{3+}}$ multiplets. A SPEX 1681 monochromator was used to filter the superfluorescence of the dye laser output. Fluorescence was measured by a SPEX 1404 double spectrometer resonantly or at the nearest long-wavelength optical transition where there was no spectral overlap with the emission from lower-lying multiplets. A Hamamatsu 943-02 photomultiplier tube with a spectral sensitivity range of 300–950 nm and a time resolution of ~ 2.5 ns was used as a photodetector. A Gated Boxcar Integrator (4420/4422, EG&G PAR) interfaced with an IBM computer, or a digital oscillocope (Tektronix 2431L) were used for the fluorescence lifetime measurements. The time resolution of the whole system was determined by the pulse width of the dye laser and was equal to ~ 10 ns. A range of dyes (Exciton Corp.) were used for direct excitation of $\mathrm{Er^{3+}}$ multiplets over the wide spectral range. The energy per pulse for different dyes varied from 100 to 300 μJ as measured by an energy radiometer (RJ-7620, Laser Precision). Thus the pumping level of the order of 10^{14} photons per pulse excluded the possibility of any induced or cooperative nonlinear processes. All measurements were done at 77 K.

IV. RESULTS AND DISCUSSION

For the $\mathrm{LiYF_4}$ crystal the excited electronic state lifetimes (τ) were measured in the crystal containing 3% concentration of $\mathrm{Er^{3+}}$ ions. The measurement of τ was made on the final stages of the kinetic decay where any concentration quenching is assumed to be neglible. These new and other earlier results of MR rates in $\mathrm{LiYF_4}$ and $\mathrm{LaF_3}$ crystals doped with $\mathrm{Nd^{3+}}$ and $\mathrm{Er^{3+}}$ ions are collected in Table I. The energy gaps $\Delta E_{\min}$ have been taken from Ref. 10. For $\mathrm{Er^{3+}}$ ions in $\mathrm{LaF_3}$ (refractive index $n \approx 1.6$) the Judd-Ofelt Ω_k intensity parameters ($\Omega_2=1.07\times10^{-20}$ cm^2, $\Omega_4=0.28\times10^{-20}$ cm^2, $\Omega_6=0.83\times10^{-20}$ cm^2) and the matrix elements $U^{(k)}$ used for the calculation of the radiative relaxation rate A_i and radiative lifetime $\tau=(\sum A_i)^{-1}$ of the $^4F_{5/2}$ multiplet were taken from Ref. 3. The parameters for $\mathrm{LaF_3{:}Nd^{3+}}$ ($\Omega_2=0.35\times10^{-20}$ cm^{-2}, $\Omega_4=2.57\times10^{-20}$ cm^2, $\Omega_6=2.50\times10^{-20}$ cm^2) were taken from Ref. 20 and for $\mathrm{LiYF_4{:}Nd^{3+}}$ (refractive index $n\approx1.46$) the parameters ($\Omega_2=1.9\times10^{-20}$ cm^2, $\Omega_4=2.7\times10^{-20}$ cm^2, $\Omega_6=5.0\times10^{-20}$ cm^2) were taken from Ref. 10. The matrix elements for the $\mathrm{Nd^{3+}}$ transitions from multiplets lying lower than $^4G_{9/2}$ were obtained from Ref. 10 and for those from multiplets higher than $^4G_{9/2}$ were provided by Dr. A. Kornienko of the Pedagogical Institute of Vitebskcity (Belorussia). The multiphonon relaxation rates were calculated from

$$W_{\mathrm{MR}}=W_{\mathrm{meas}}-A , \tag{23}$$

where $W_{\mathrm{meas}}=1/\tau$ is the measured decay rate of the excited multiplet.

The point-charge nonlinear relaxation theory of Ref. 15 is used as a first approximation for the analysis of the intermultiplet radiationless transition rates and their dependencies on the type of multiplet and the number of phonons n. The η parameters of this theory were determined for each intermultiplet radiationless transition and are presented in Table II. Only processes with the minimal integer number of phonons $n_{\min}$ have been taken into account ($n_{\min}=\Delta E/\hbar\omega_{\max}$). The maximum phonon energies used [$\hbar\omega_{\max}=570$ cm^{-1} in $\mathrm{LiYF_4}$ (Ref. 21) and 400 cm^{-1} in $\mathrm{LaF_3}$ (Ref. 22)] were in good agreement with the phonon stimulated W_{MR} temperature dependencies (see, for example Ref. 6). The processes with $n_{\min+1}$, $n_{\min+2}$, etc., were not considered as according to Eq. (4)

TABLE I. Radiative and nonradiative relaxation rates for some multiplets of Nd^{3+} and Er^{3+} ions in $LiYF_4$ and LaF_3 crystals.

Crystal	Multiplet	$E_{\min}$ (cm^{-1})	Ath (s^{-1})	Ref.	W_{meas} (s^{-1})	Ref.	W_{MR} (s^{-1})
$LiYF_4$:Er^{3+}	$^4F_{5/2}$	1561	295	31	$(1.88\pm0.23)\times10^7$	This work	$(1.88\pm0.23)\times10^7$
	$^4G_{11/2}$	1656	2 950	31	$(2.05\pm0.65)\times10^7$	This work	$(2.05\pm0.65)\times10^7$
	$^2H_{9/2}$	2217	395	31	$(8.05\pm0.85)\times10^4$	This work	$(8.02\pm0.85)\times10^4$
	$^4F_{9/2}$	2656	800	32	$(8.95\pm0.48)\times10^3$	This work	$(8.15\pm0.48)\times10^3$
	$^4S_{3/2}$	2956	$(1.33\pm0.03)\times10^3$	32	$(1.63\pm0.09)\times10^3$	24	$(3\pm0.6)\times10^2$
$LiYF_4$:Nd^{3+}	$^4G_{7/2}$	1381	5001	This work	8.33×10^7	8	8.33×10^7
	$^4D_{3/2}$	1752	21 687	This work	9.09×10^5	8	8.87×10^5
	$^2P_{3/2}$	2239	2 039	This work	$(3.46\pm0.89)\times10^4$	8	$(3.26\pm0.89)\times10^4$
LaF_3:Er^{3+}	$^4F_{5/2}$	1582	1645	This work	$(1.52\pm0.46)\times10^6$	This work	$(1.52\pm0.46)\times10^6$
	$^4G_{11/2}$	1662	6.54×10^3	3	$(3.34\pm0.11)\times10^5$	This work,1	$(3.28\pm0.11)\times10^5$
	$^2H_{9/2}$	1853	1.47×10^3	3	$(1.11\pm0.6)\times10^4$	3,4	$(0.97\pm0.18)\times10^4$
	$^4I_{9/2}$	2022	48	3	$(7.57\pm1.12)\times10^3$	3,4	$(7.53\pm1.12)\times10^3$
	$^4F_{9/2}$	2698	535	3	$(1.43\pm0.13)\times10^3$	3,4	$(8.95\pm1.3)\times10^2$
LaF_3:Nd^{3+}	$^4F_{9/2}$	1121	1 639	33	1.54×10^8	6	1.54×10^8
	$^4G_{5/2}+{}^2G_{7/2}$	1201	7 299	33	3.43×10^7	6	3.43×10^7
	$^4G_{7/2}$	1546	3 723	33	9.05×10^6	6	9.05×10^6
	$^2P_{3/2}$	2373	1 712	This work	$(2.31\pm0.06)\times10^3$	34	$(5.98\pm0.06)\times10^2$
	$^4D_{3/2}$	1891	22 520	This work	$(2.6\pm0.22)\times10^4$	34	$(3.48\pm2.2)\times10^3$

the MR probability $W_{\alpha-\alpha'}$ decreases 1 to 2 (or more) orders of magnitude when n is increased by one. The matrix elements $U^{(k)}$ needed for the μ_{lk} parameters, and the values of the Stark splittings of the multiplets of Nd^{3+} and Er^{3+} ions, have been taken from Refs. 10 and 23. In the case of the $^4D_{3/2}$ multiplet of Nd^{3+}, the $U^{(k)}$ matrix elements were provided by Dr. Kornienko. The calculated values of the μ_{lk} parameters for each intermultiplet radiationless transition and the effective number of inter-Stark transitions g are also listed in Table II. The calculation of the relative population of the αth Stark level for the upper A multiplet was done with a Boltzman distribution at 77 K. Temperature stimulation of MR has not been considered as investigations of temperature dependencies of W_{MR} in similar crystals doped with RE ions have shown that this process is not observed at tempera-

TABLE II. Parameter values for the point-charge nonlinear relaxation theory, assuming a harmonic approximation for the crystal lattice vibrations, for $LiYF_4$ and LaF_3 crystals doped with Er^{3+} and Nd^{3+} ions. The asterisk indicates those transitions for which μ_{32} is not considered as having the largest contribution.

Crystal	Transition	$\Gamma_{\min}$	g	μ_{32}	μ_{34}	μ_{36}	η (10^4)	$\bar{\eta}$ (10^4)
$LiYF_4$:Er^{3+}	$^4F_{5/2}\rightarrow{}^4F_{7/2}$	3	2.87	2.92×10^{-3}	1.33×10^{-3}	3.43×10^{-3}	1.94	2.32
	$^4G_{11/2}\rightarrow{}^2H_{9/2}$	3	0.75	4.61×10^{-3}	1.26×10^{-3}	1.75×10^{-3}	2.70	
	$^2H_{9/2}\rightarrow{}^4F_{3/2}+{}^4F_{5/2}$	4	1.76	4.17×10^{-4}	1.31×10^{-3}	5.0×10^{-4}	2.98	
	$^4F_{9/2}\rightarrow{}^4I_{9/2}$	5	2.34	1.79×10^{-3}	7.76×10^{-5}	1.96×10^{-4}	5.65	
*	$^4S_{3/2}\rightarrow{}^4F_{9/2}$	6	5	0	1.59×10^{-6}	9.3×10^{-4}	5.43	
$LiYF_4$:Nd^{3+}	$^4G_{7/2}\rightarrow{}^4G_{5/2}+{}^2G_{7/2}$	3	3.52	1.7×10^{-3}	6.16×10^{-3}	2.72×10^{-3}	2.37	2.37
	$^4D_{3/2}\rightarrow{}^2P_{3/2}$	4	2	1.38×10^{-3}	0	0	4.62	
	$^2P_{3/2}\rightarrow{}^2D_{5/2}$	4	1	4.01×10^{-4}	6.3×10^{-6}	0	2.46	
LaF_3:Er^{3+}	$^4F_{5/2}\rightarrow{}^4F_{7/2}$	4	0.7	2.92×10^{-3}	1.33×10^{-3}	3.43×10^{-3}	6.05	5.03
	$^4G_{11/2}\rightarrow{}^2H_{9/2}$	4	0.52	4.61×10^{-3}	1.26×10^{-3}	1.75×10^{-3}	4.0	
*	$^2H_{9/2}\rightarrow{}^4F_{3/2}$	5	2	0	7.51×10^{-4}	3.47×10^{-4}	7.27	
*	$^4I_{9/2}\rightarrow{}^4I_{11/2}$	6	6	3.42×10^{-5}	7.31×10^{-4}	2.08×10^{-3}	8.61	
	$^4F_{9/2}\rightarrow{}^4I_{9/2}$	7	2	1.79×10^{-3}	7.76×10^{-5}	1.96×10^{-4}	8.63	
LaF_3:Nd^{3+}	$^4F_{9/2}\rightarrow{}^4F_{7/2}+{}^4S_{3/2}$	3	3.65	2.24×10^{-3}	1.54×10^{-3}	9.86×10^{-4}	3.64	3.64
	$^4G_{5/2}+{}^2G_{7/2}\rightarrow{}^2H_{11/2}$	3	0.47	1.34×10^{-4}	3.54×10^{-6}	6.34×10^{-3}	8.93	
	$^4G_{7/2}\rightarrow{}^4G_{5/2}+{}^2G_{7/2}$	4	1.68	1.7×10^{-3}	6.16×10^{-3}	2.72×10^{-3}	6.24	
	$^4D_{3/2}\rightarrow{}^2P_{3/2}$	5	1.86	1.38×10^{-3}	0	0	4.3	
	$^2P_{3/2}\rightarrow{}^2D_{5/2}$	6	0.68	4.01×10^{-4}	6.3×10^{-6}	0	7.07	

tures below 100 K.[1,4,6,24,25] The mean values of the kth power of the radius vector of the optical electron ($\bar{\xi}^k$) were taken from Ref. 26. For Nd^{3+} these values are $\bar{\xi}^2=0.283$ Å^2, $\bar{\xi}^4=0.188$ Å^4, and $\bar{\xi}^6=0.272$ Å^6 and for Er^{3+} the values are approximately 2–3 times less and equal to 0.187 Å^2, 0.0883 Å^4, and 0.0874 Å^6, respectively. The minimum mean distance R_0 between the RE ion and the nearest-neighboring F^- ions and their coordination number z, have been taken from Refs. 19, 27, and 28. These values are $R_0=2.27$ Å and $z=8$ for $LiYF_4$ and $R_0=2.46$ Å and $z=5$ for LaF_3.

Using Eqs. (4), (5), (21), and (22) and the measured values of the MR rates (Table I), the constant η parametrizing the strength of the electron-phonon coupling in the point-charge nonlinear model was obtained for each transition. It is seen from Table II that an increase of n from 3 to 5 causes a 2.1–2.9 times increase of η in $LiYF_4$:Er^{3+}. Also, the increase of n from 4 to 7 in LaF_3:Er^{3+} causes a ~ 2 times increase of η. Thus the predictions of the point-charge nonlinear theory are not in good agreement with the experimental rates. Because of the η^n factor in the calculated W_{MR} rate the ~ 2 times increase in η for Er^{3+} in LaF_3 leads to a 40 times increase in W_{MR} in the 7-phonon ${}^4F_{9/2} \to {}^4I_{9/2}$ transition over a typical 4-phonon transition. This increase of the η parameter with n more than 3–4 for Er^{3+} ions in $LiYF_4$ and LaF_3 crystals is in good agreement with the enhanced values of MR relaxation rates measured for Er^{3+} and Ho^{3+} ions in the case of large energy gaps ($\Delta E > 2000$ cm^{-1}) (Refs. 4 and 9) in comparison with Nd^{3+} ions and small energy gaps ($\Delta E \leq 2000$ cm^{-1}).[8] For Nd^{3+} ion in LaF_3 the smooth increase in the parameter η is not observed (Table II). Therefore it is appropriate to trace the functional dependence of Eq. (4) on the number of phonons n, and then try to compare it with the functional behavior of the experimental MR rates. With that end in view Eq. (4) is transformed as follows:

$$W_{\alpha-\alpha'}(0)=D_1\eta^n \sum_{k=2,4,6} \mu_{3k}(AA')(\bar{\xi}^k/R_0^k)^2 c'_k(n) , \tag{24}$$

where $D_1=(ze^2e_s^2)/(c\bar{v}\hbar^2R_0^2)$ is a constant that depends on the type of crystal. From Eq. (24) it is clear that the n dependence of $W_{MR}(n)$ is only determined by the terms η^n and $c'_k(n)$ [see Eq. (7)]. Additionally, for a more simple functional dependnece of Eq. (24) on n, the parameter μ_{3k} could be considered as k independent, i.e., $\mu_{32}=\mu_{34}=\mu_{36}$. In that case we omit the k index and factor out μ_3 from the sum in Eq. (24):

$$W_{\alpha-\alpha'}(0)=D_1\eta^n\mu_3(AA') \sum_{k=2,4,6} (\bar{\xi}^k/R_0^k)^2 c'_k(n) . \tag{25}$$

In this form it is not difficult to analyze the dependence of the last term of Eq. (25) on n.

Figure 1 shows the n dependence of $c'_k(n)$ and the product $(\bar{\xi}^k/R_0^k)^2c'_k(n)$ for $k=2$, 4, and 6 using the data for the $LiYF_4$:Er^{3+} crystal. Also shown in Fig. 1 is the sum $\sum_k(\bar{\xi}^k/R_0^k)^2c'_k(n)$. The results show that $c'_6(n)$ and $(\bar{\xi}^6/R_0^6)^2c'_6(n)$ are closest to a straight line on the logarithmic scale used, indicating a simple n^α dependence. The maximum deflection from linearity is observed for $k=2$ at $n>6$. The crystal- and ion-dependent term $(\bar{\xi}^k/R_0^k)^2$ decreases by approximately two orders of magnitude with an increase in k from 2 to 4 and from 4 to 6. Therefore with approximately equal μ_{3k} parameters ($\mu_{32}\approx\mu_{34}\approx\mu_{36}$) and for a small number of phonons ($n=3$–4), the major contribution to the relaxation rate comes from the term with $k=2$.

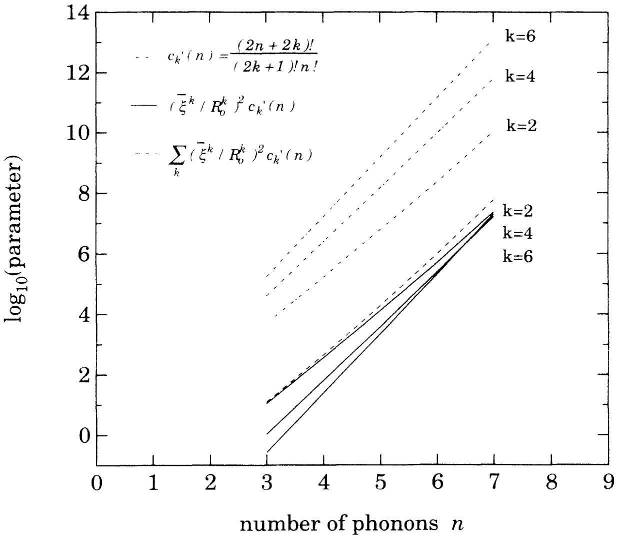

FIG. 1. The dependencies of some parameters of the point-charge nonlinear relaxation model versus the number of phonons n participating in the radiationless transition.

In the case of large numbers of phonons ($n=6$–7) the influence of all k terms becomes comparable. Thus in the point-charge nonlinear theory that considers η fixed, the additional terms in the sum of Eq. (25) give larger calculated MR rates and a reduction of the slope of the $W_{MR}(n)$ dependence on the logarithmic scale at $n>5$.

For all Nd^{3+} transitions and most Er^{3+} transitions (except those marked by an asterisk in Table II) the μ_{32} parameter has the largest influence on the MR rates when compared to μ_{34} and μ_{36}. That means that the quadrupole term $\bar{V}_2\xi^2$ of the expansion of the dynamical part of the crystal field ($\bar{V}=\bar{V}_0+\bar{V}_2\xi^2+\bar{V}_4\xi^4+\bar{V}_6\xi^6+\cdots$) has the dominant contribution to the multiphonon nonradiative transitions for these ions in both crystals.

For a comparison between the measured MR rates and those calculated from the point-charge nonlinear model, it is convenient to use a normalized transition rate. The experimental normalized MR transition rates were determined by dividing the measured MR rate by the product of the most significant μ_{3k} parameter and g, i.e., $W_{MR}/(\mu_{3k}*g)$. The theoretical normalized transition rate is calculated assuming $\mu_{34}=\mu_{36}=0$ and using $\eta=\bar{\eta}$ where $\bar{\eta}$ is a kind of average η determined for a given crystal only from those transitions involving a minimal number of phonons (3 or 4). The small number of phonons is chosen, since as we shall show later, the influence of covalent bonding is minimal here. The results of the measured and theoretical normalized MR transition rates for several intermultiplet transitions of Er^{3+} and Nd^{3+} ions in LaF$_3$ and LiYF$_4$ crystals are presented in Fig. 2

The n dependence of the theoretical $W_{\mathrm{MR}}(n)$ rate is determined by the $\bar{\eta}$ parameter and the last term of Eq. (25). For LiYF$_4$ approximately equal $\bar{\eta}$ values were obtained for Er^{3+} and Nd^{3+} ions (Table II). In LaF$_3$ this parameter was slightly different for the two ions but here transitions involving a different number of phonons ($n=3$ for Nd^{3+} and $n=4$ for Er^{3+}) were used in the determination of $\bar{\eta}$. It was found that $\bar{\eta}$ was approximately 1.6 times larger in LaF$_3$ than in LiYF$_4$. This means that $W_{\mathrm{MR}}(n)$ has a greater slope for LiYF$_4$ on the logarithmic scale of Fig. 2.

Since $\eta=u_0^2/R_0^2$ and taking into account $R_0(\mathrm{LaF_3})>R_0(\mathrm{LiYF_4})$, a larger amplitude of zero-order oscillations is observed in the LaF$_3$ crystal ($\bar{\eta}=3.64\times10^{-4}$ and $u_0=4.69\times10^{-2}$ Å) in comparison with LiYF$_4$ ($\bar{\eta}=2.35\times10^{-4}$ and $u_0=3.77\times10^{-2}$ Å). It is reasonable to consider the η parameter [Eq. (4)] as an intensity for the dynamical part of crystal field while the S parameter of the linear MR relaxation theory [Eq. (3)] reflects the strength of the static electron-phonon coupling. Thus LaF$_3$ has the larger dynamical part of the crystal field or larger transient electron-phonon coupling than LiYF$_4$. Another conclusion can be drawn from the $W_{\mathrm{MR}}(\Delta E_{\min})$ dependencies of the Er^{3+} ion in LaF$_3$ and LiYF$_4$ crystals (see Table I) using the linear approximation of the MR theory. The slope α of the energy-gap dependence of $W_{\mathrm{MR}}(\Delta E)$ is smaller in LaF$_3$ ($\alpha=2.61\times10^{-3}$) than in LiYF$_4$ ($\alpha=3.45\times10^{-3}$). Then

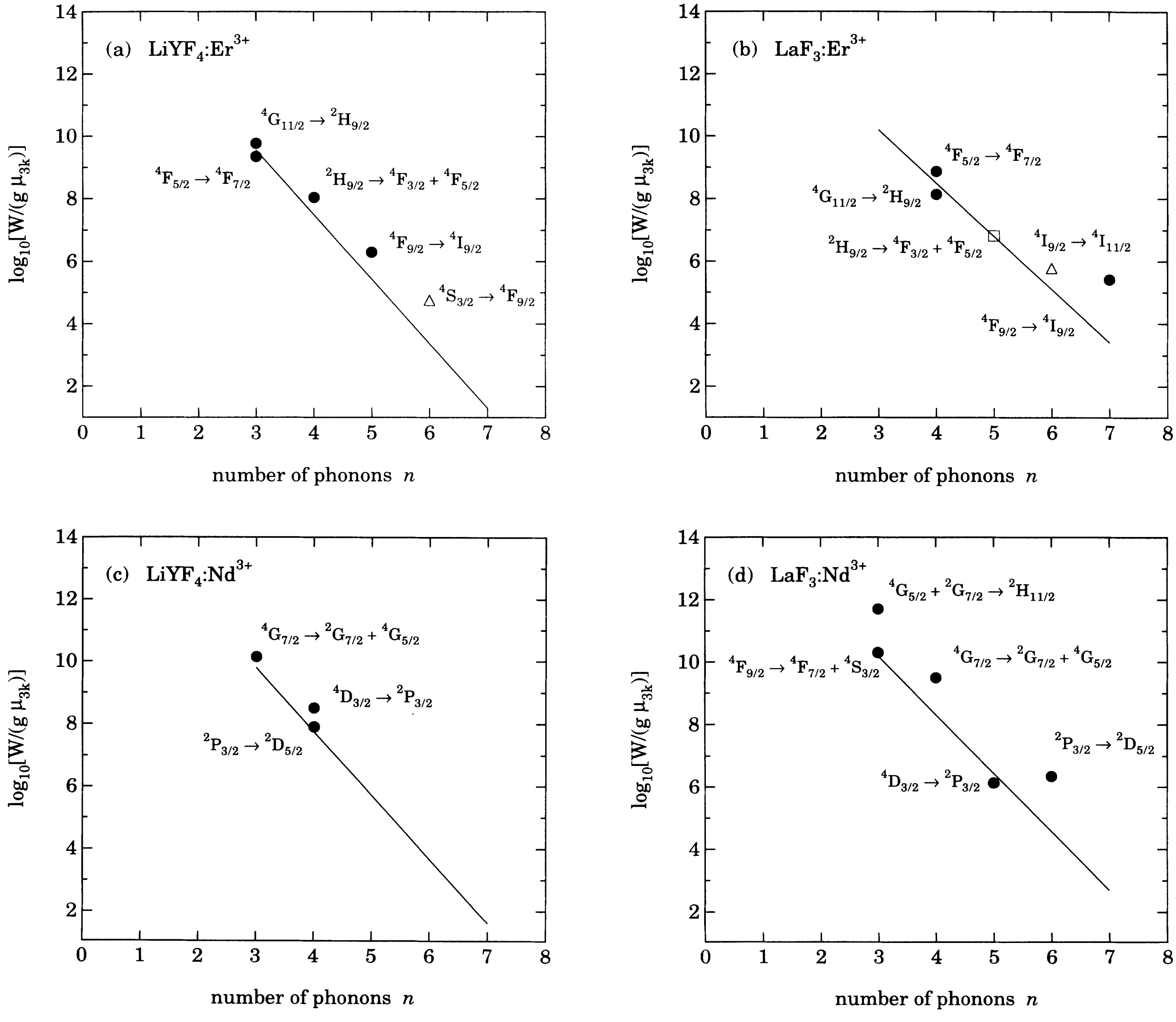

FIG. 2. The experimental values of MR rates (W_{MR}) divided by ($g\mu_{3k}$) and theoretically calculated dependencies normalized to $g\mu_{3k}$ (for $\mu_{34}=\mu_{36}=0$) in the point-charge nonlinear harmonic relaxation theory vs number of phonons n (solid lines): (a) LiYF$_4$:Er^{3+}, $\bar{\eta}=2.32\times10^{-4}$; (b) LaF$_3$:Er^{3+}, $\bar{\eta}=5.03\times10^{-4}$; (c) LiYF$_4$:Nd^{3+}, $\bar{\eta}=2.37\times10^{-4}$ (d) LaF$_3$:Nd^{3+}, $\bar{\eta}=3.64\times10^{-4}$. Solid circles W_{MR}/μ_{32}, hollow squares W_{MR}/μ_{34}, hollow triangles W_{MR}/μ_{36}.

using Eq. (3) it can be concluded that the S parameter and hence, the strength of the static electron-phonon coupling is larger in LaF_3 ($S=n\times0.13$) than in $LiYF_4$ ($S=n\times0.051$). Thus, in our opinion, it is necessary to be careful when determining the strength of the static electron-phonon coupling (parameter S) from the measurements of MR rates in the case of extremely weak electron-phonon coupling as other relaxation mechanisms might be responsible for the dominant contribution to the MR probability. According to Ref. 15 S is proportional to the square of the sum of the absolute values of the Stark splitting, $S\sim|\Delta\epsilon_{st}(\alpha)+\Delta\epsilon_{st}(\alpha')|^2$ of the multiplets participating in the transition. Thus the conclusion here that S is larger in LaF_3 is in contradiction with the fact that for Nd^{3+} multiplets the Stark splitting, that is the static part of crystal field, is comparable in $LiYF_4$ and in LaF_3 (Ref. 29) and even slightly larger for some multiplets in $LiYF_4$.

It can be seen from Fig. 2 that the experimental MR probabilities tend to be larger than the theoretical dependence, especially for those transitions with larger numbers of phonons. In the formalism of the point-charge nonlinear model this means that for those transitions with enhanced values, the η parameter is larger than average. For example, in $LiYF_4{:}Er^{3+}$ the η parameter changes only by 50% for 3–4-phonon transitions, but is observed to increase 3.8 times for 5–6-phonon processes. A similar situation is also observed in $LaF_3{:}Er^{3+}$. Thus the influence of the other relaxation mechanisms on the MR probability, for example, covalent-nonlinear (exchange) and/or the influence of anharmonicity of lattice vibrations might be important for transitions with $n>3$–4.

First consider the additional influence of the covalence of the electron-ligand bonding. The ratios of $W_k^{ex}(n)/W_k^{pc}(n)$ for $LiYF_4{:}Er^{3+}$ have been calculated from Eqs. (12) to (19) and are listed in Table III and presented in Fig. 3. The crystal-field parameters of the exchange interaction model that are required for the calculation of the $W_k^{ex}(n)/W_k^{pc}(n)$ ratios are given in Table IV. For the G_ν parameters, that are characteristic of the crystal, the single-parameter approximation was used ($G_s=G_\sigma=G_\pi$) and the value was determined from a best fit of the calculated Stark splitting of the $^4I_{15/2}$ multiplet of Er^{3+} in $LiYF_4$. The S_ν^0 parameter characterizes the overlap integral of the Er^{3+} optical $4f$ electron with the n orbital of the F^- electron. The α_ν parameter is given in atomic units and describes the extent of the overlap of the wave functions of the $4f$ electron and the ligand.

TABLE III. The values of the ratio $W_k^{ex}(n)/W_k^{pc}(n)=(B_k^0/a_k^0)^2\beta_k$ in $LiYF_4{:}Er^{3+}$ calculated from Eqs. (13) to (19).

$k \backslash n$	2	3	4	5	6	7
2	0.564	1.756	4.187	8.0	12.85	37.2
4	16.2	24.9	33.0	38.6	40.6	39.1
6	42.7	37.8	34.3	30.8	26.3	20.9

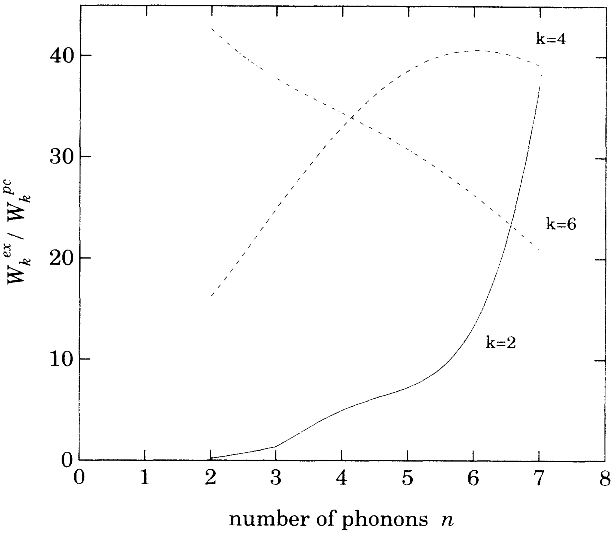

FIG. 3. The ratio $W_k^{ex}(n)/W_k^{pc}(n)$ of MR probabilities due to the exchange and point-charge interactions versus the number of phonons n participating in radiationless transition for $k=2$, 4, and 6.

Having equated the experimentally measured MR rates to the right-hand side of Eq. (20) and considering Eq. (22), the new η parameters and the ratios of the partial MR probabilities (W^{ex}/W^{pc}) for all radiationless transitions in $LiYF_4{:}Er^{3+}$ have been calculated and are listed in Table V.

The increase of η by the factor of 2.91 in the point-charge nonlinear model when n changed from 3 to 5 (Table II) is now only an increase of 1.81 when both mechanisms have been taken into consideration (Table V). Also, now that covalence has been considered, the averaged η for 3-phonon transitions ($\bar{\eta}=1.53\times10^{-4}$) has become equal to the value of η for a 4-phonon transition ($\bar{\eta}=1.56\times10^{-4}$). This last point shows that accounting for both relaxation mechanisms (point-charge and exchange) in the harmonic approximation produces a good agreement with the experimental MR rates for a 4-phonon transition in $LiYF_4{:}Er^{3+}$.

It can be seen from Fig. 2(a) for $LiYF_4{:}Er^{3+}$ that the measured MR rates show a smooth deviation to the enhanced valus from the theoretical line with increasing n. The reason for this is the small contribution from the μ_{34} and μ_{36} parameters in the case of nonradiative transitions from the $^4F_{9/2}$ and $^2H_{9/2}$ levels. This means that

TABLE IV. Crystal-field parameters for the exchange interaction model. All values were obtained from Ref. 19.

$G_s=G_\sigma=G_\pi=7.6$
$S_s^0=6.08$
$S_\sigma^0=0.65$
$S_\pi^0=1.85$
$\alpha_s=1.509$
$\alpha_\sigma=0.887$
$\alpha_\pi=1.233$
$R_0=2.27$ Å

TABLE V. Parameters values for the point-charge nonlinear and covalent-nonlinear relaxation theories that have been determined for LiYF$_4$:Er^{3+} from the experimental MR probabilities.

Transition	η (10^4) without covalence	η (10^4) with covalence	$W^{\text{ex}}/W^{\text{pc}}$	Number of phonons n
$^4F_{5/2}\rightarrow{}^4F_{7/2}$	1.94	1.24	2.9	3
$^4G_{11/2}\rightarrow{}^2H_{9/2}$	2.70	1.82	2.32	3
$^2H_{9/2}\rightarrow{}^4F_{3/2}+{}^4F_{5/2}$	2.98	1.56	12.6	4
$^4F_{9/2}\rightarrow{}^4I_{9/2}$	5.65	2.25	8.5	5
* $^4S_{3/2}\rightarrow{}^4F_{9/2}$	5.43	3.13	26.3	6

the contribution of the μ_{32} parameter prevails over the other μ_{3k} terms (since $W^{\text{ex}}\sim\sum_k\mu_{3k}$) and the $W_2^{\text{ex}}(n)/W_2^{\text{pc}}(n)$ term contributes the most to the MR probabilities. Figure 3 shows that for $k=2$ the exchange interaction has a very pronounced influence for the larger values of n (and only a small influence for $n=3$) and thus the measured MR rates are found well above those predicted by the point-charge nonlinear model theoretical line [see, for example, Fig. 2(a)].

For multiplets with small μ_{32} values, for example, $^4I_{9/2}$ and $^4S_{3/2}$ of Er^{3+} and $^4G_{5/2}$ of Nd^{3+}, the other $W_k^{\text{ex}}(n)/W_k^{\text{pc}}(n)$ terms may make comparable contributions to the MR probabilities. These terms would cause a larger total contribution of the exchange interaction to the total MR rates and we would expect the measured values of W_{MR} to be larger than those predicted by the point-charge model theory line. This may even be significant at small n as in the case of $^4G_{5/2}$ for Nd^{3+}.

For the $^4F_{9/2}$ and $^4G_{7/2}$ multiplets of Nd^{3+} in LaF$_3$ the μ_{32} parameters are approximately equal and the relative size of the other μ_{3k} parameters should be examined when comparing MR rates. In $^4G_{7/2}$ the μ_{34} and μ_{36} are approximately 4 times and 2.75 times larger, respectively, than the equivalent parameters in $^4F_{9/2}$. From the data in Table III which were determined for LiYF$_4$:Er^{3+} but should be valid for LaF$_3$:Nd^{3+}, it can be seen that for $k=4$ the influence of the exchange interaction increases by a factor of 1.3 for a 4-phonon transition compared with a 3-phonon transition, whereas for $k=6$ the influence decreases by a factor of 1.1. Thus overall it is expected that the exchange interaction would have more influence on the $^4G_{7/2}$ multiplet than $^4F_{9/2}$ which should therefore have a W_{MR} rate that deviates higher from the point-charge theory line. Examination of Fig. 2(d) shows that this is indeed the case.

A special comment is required for the $^2P_{3/2}\rightarrow{}^2D_{5/2}$ transition in LaF$_3$:Nd^{3+}. According to Table II all the μ_{3k} parameters are small and thus it is expected that the measured MR rate should be close to the point-charge theory line as the influence of the exchange interaction is small. However, this is not the case as the data point lies ~ 1.5 orders of magnitude higher [Fig. 2(d)]. It may be such that this transition proceeds via a 5-phonon rather than 6-phonon process requiring a phonon energy $\hbar\omega=470$ cm^{-1}. Such a value of $\hbar\omega$ may not be unreasonable considering the vibronic spectra of the LaF$_3$ crystal.[30]

For LaF$_3$:Er^{3+} there is no measured MR rate for a $n=3$ phonon transition. Thus the value of $\bar{\eta}=5.03\times10^{-4}$ used for the point-charge theory line was determined from the data for $n=4$ transitions. According to Table III there is a significant increase in the influence of the exchange interaction between $n=3$ and $n=4$ transitions, especially for $k=2$. Thus the value of $\bar{\eta}$ used is probably larger than the one that would be determined if only the point-charge interaction was present. If a smaller value had been used then the slope of the point-charge theory line on Fig. 2(b) would have been greater than that shown and thus the deviation of the measured values would have been greater at large n.

Finally it can be concluded that the exchange interaction between the rare-earth ion and ligands has less influence for transitions that involve a small number of phonons of n. The addition of the exchange interaction qualitatively explains the enhanced MR rates measured for some transitions of Er^{3+} and Nd^{3+} ions in LiYF$_4$ and LaF$_3$ crytals. The increase of η required to match the prediction of the point-charge and exchange interactions with the data at large n, may be attributable to anharmonicity of the lattice vibrations. Unfortunately, at this time there is no theory that will consider all three mechanisms simultaneously.

V. CONCLUSIONS

A point-charge nonlinear relaxation mechanism that assumes a harmonic approximation for the lattice vibrations successfully describes the variation of the MR rates with the number of phonons. The nth term of the expansion of the electron-phonon interaction Hamiltonian plays the crucial role in an n-phonon radiationless transition. Specifically an increase in the number of phonons from n to $n+1$ leads to a decrease in W_{MR} by two orders of magnitude. The enhancement of the measured MR rates for $n\geq6$ is also qualitatively explained within the framework of this relaxation mechanism. The change in slope on the logarithmic scale for $W_{\text{MR}}(n)$ as a function of n for Nd^{3+} and Er^{3+} ions in different crystal lattices is determined primarily by the variation of the strength of the dynamical part of the crystal field (the η parameter). The results show that η is larger in LaF$_3$ than in LiYF$_4$ implying a larger amplitude of zero vibrations of the lattice in LaF$_3$ versus LiYF$_4$.

The addition of the exchange interaction between the rare-earth ion and ligands to the nonlinear relaxation theory increases the MR probability for most transitions of Nd^{3+} and Er^{3+} ions in both crytals, which is in good agreement with experimental rates. Also the additional consideration of the exchange mechanism qualitatively explains the decreasing slope on the logarithmic scale of the measured W_{MR} dependencis versus the number of phonons n.

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