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Multiphonon sideband intensities in rare earth ions in crystal

Konstantin K. Pukhov[a,*], Tasoltan T. Basiev[a], Johann Heber[b], Sergey Mirov[c], Francois Auzel[d]

[a]*Laser Materials and Technologies Research Center of General Physics Institute, 38 Vavilov Street, Block D, 117942, GSP-1, Moscow, Russia*
[b]*Institute of Solid State Physics, Darmstadt University of Technology, Hochschulstr. 8, D-64289 Darmstadt, Germany*
[c]*The University of Alabama at Birmingham, 1300 University Boulevard, Birmingham, AL 35294-1170, USA*
[d]*GOTR, UPR211, CNRS, Laboratoire de Physicochimie des Materiaux, 1 Pl. A-Briand, 92195 Meudon Cedex, France*

Abstract

Intermultiplet transitions involving emission (or absorption) of one photon and *n* phonons are theoretically investigated in trivalent rare earth (RE) ions in crystals. Transitions are induced by joint action of electromagnetic field and high-order optical anharmonicity (M-process). Hence, this work extends Judd's study of one photon–one phonon transitions to the multiphonon case. The processes under consideration give rise to the Stokes and anti-Stokes multiphonon sidebands of light emission or absorption. Besides, these processes can significantly increase the rate of intermultiplet transitions in the presence of stimulated emission. As far as we know the problem of multiphonon sidebands have not been considered previously in the theory of M-processes. Here we obtained general expression for transition probabilities. In doing this we used the crystal field model that takes into account both Coulomb and non-Coulomb interactions of 4f-electrons with ligands. (Previously we used this model for the calculation of multiphonon rates in RE ions.) The "electronic part" of obtained expression is presented exactly in the same form as the well-known Judd–Ofelt expression for radiative transition probability between multiplets. A simplified form of general expression is proposed. Other mechanisms of photon–phonon transitions are briefly discussed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Multiphonon; Sideband; Rare earth ion

1. Introduction

In this paper we present results of the theoretical study of intermultiplet photon–phonon transitions in RE ions. These transitions are induced by joint action of electromagnetic field and high-order optical anharmonicity. Hence, this work extends Judd's study [1] of one photon–one phonon transitions to the multiphonon case. The processes under consideration give rise to the Stokes and anti-Stokes multiphonon sidebands of light emission or absorption. Besides, these processes can significantly increase the rate of intermultiplet transitions in the presence of stimulated emission.

Here we obtained general expression for transition probabilities. In doing this we used the crystal field model that takes into account both Coulomb and non-Coulomb interactions of 4f-electrons with ligands.

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* Corresponding author. Tel.: + 7-95-1328376; fax: + 7-095-1350270.

E-mail address: pukhov@lst.gpi.ru (K.K. Pukhov)

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The probability of induced absorption transition from initial state $|\, i\,)$ with energy E_i to final state $|\, f\,)$ with energy E_f ($E_i < E_f$) can be written as

$$W = \frac{2\pi\alpha\chi P}{\hbar}\int_{-\infty}^{\infty} \exp\,[\mathrm{i}(\Delta - \Omega)t] \times \langle d_q(t) d_{q'}(0)\rangle e_q e_{q'} \mathrm{d}t, \qquad (1)$$

where $\alpha = e^2/\hbar c$ is the fine-structure constant; $\chi = [(\varepsilon + 2)/3]^2/\sqrt{\varepsilon}$ ($\sqrt{\varepsilon}$ is the refractive index); P is the intensity of incident light; Ω is the light frequency; e_q are components of light polarization vector; $\Delta = (E_f - E_i)/\hbar$. In the expression for correlation function $\langle d_q(t) d_{q'}(0)\rangle$ the symbol $\langle \cdots \rangle$ denotes an average on lattice vibrations; $d_q = (i\,|\, D_q \,|\, f)$; $d_{q'} = (f\,|\, D_{q'}\,|\, i)$; $\boldsymbol{D} = \boldsymbol{p}/e$, $\boldsymbol{p}$ is the 4f-electrons dipole moment; $d_q(t) = \exp\,(\mathrm{i}H_{\mathrm{L}}t/\hbar)\, d_q \exp\,(-\mathrm{i}H_{\mathrm{L}}t/\hbar)$; H_{L} is the lattice vibrations Hamiltonian. The probability of induced radiation transition (W_{em}) is related to the probability of the induced absorption transition ($W_{\mathrm{abs}} = W$) by the equation

$$W_{\mathrm{em}}/W_{\mathrm{abs}} = \exp\,[\hbar\,(\Delta - \Omega)/kT]. \qquad (2)$$

The probability of spontaneous emission in frequency region $[\Omega, \Omega + \mathrm{d}\Omega]$ can be written as $W_{\mathrm{sp}}(\Omega) = w\,(\Omega)\,\mathrm{d}\Omega$ with

$$w\,(\Omega) = \frac{2\alpha\varepsilon\chi}{3\pi c^2}\,\Omega^3 \int_{-\infty}^{\infty} \times \exp\,[\mathrm{i}\,(\Delta - \Omega)t] \sum_q \langle d_q(t) d_{-q}(0)\rangle\, \mathrm{d}t. \qquad (3)$$

In Eqs. (1)–(3) the magnitude $\hbar\,(\Delta - \Omega)$ constitutes the energy which the crystal obtains or loses. When $\Delta < \Omega$ ($\Delta > \Omega$) the expression (1) gives the intensity of the Stokes (anti-Stokes) wing of absorption band. The mechanism considered here is sometimes called M-process [2,3].

In order to proceed with the W and W_{sp} calculation we will use an "exchange–charge" model [4] of the crystal field. The crystal field is considered in this model as $H = H_{\mathrm{M}} + H_{\mathrm{E}}$, where H_{M} is the Coulomb interaction of 4f-electrons with a field of point charges (H^{pc}) and that of the dipole moments due to the ligands. The non-Coulomb Hamiltonian

$$H_{\mathrm{E}} = \sum_s \sum_k B_k\,(r_s) \sum_m Y^*_{km}\,(\boldsymbol{r}_s) \sum_a Y_{km}\,(\boldsymbol{\xi}_a) \qquad (4)$$

($\boldsymbol{r}_s$ and $\boldsymbol{\xi}_a$ are the instantaneous radius vectors of sth ligand and ath 4f-electron, respectively), deals with interaction that is mainly due to the overlap of electron wave function with wave functions of ligands and includes the corrections to Coulomb interaction resulting from the spatial distribution of ligand electronic charge, the energy of exchange interaction, and contributions from the charge transfer states. Previously we used this model and correlation function method for the calculation of rates of the multiphonon transition [5–7].

2. Coulomb interaction contribution to muiltiphonon sideband

Here we consider the contribution to multiphonon sideband arising from the modulation of Coulomb field by crystal vibrations. In this case

$$\begin{aligned} &\langle d_q\,(t)\, d_{q'}\,(0)\rangle \\ &\quad = (-1)^{q+q'} \sum_{km\lambda} \sum_{k'm'\lambda'} (-1)^m\, [\lambda]\, [\lambda'] \\ &\quad \times \begin{pmatrix} 1 & \lambda & k \\ q & -m-q & m \end{pmatrix} \cdot \begin{pmatrix} 1 & \lambda' & k' \\ -q' & -m'+q' & m' \end{pmatrix} \\ &\quad \times (i\,|\, U^{(\lambda)}_{m+q} |\, \mathrm{f}\,)_{4\mathrm{f}}\, (f\,|U^{(\lambda')}_{-m'+q'}\,|i)_{4f}\, \Xi\,(k, \lambda) \Xi\,(k', \lambda') \\ &\quad \times \langle A_{km}(t) A^*_{k'm'}(0)\rangle. \end{aligned} \qquad (5)$$

The notation of Eq. (5) follows Judd in Ref. [1]. Subscript 4f in matrix elements of Eq. (5) denotes that operator $U^{(\lambda)}_{p+q}$ connect states of 4f-configuration, and $[\lambda] = 2\lambda + 1$ ($\lambda = 2, 4, 6$). Expressions for A_{km} in point charge model are given by Eq. (21) in Judd paper [1]. Using this expression we obtain

$$\begin{aligned} &\langle A_{km}(t) A^*_{k'm'}(0)\rangle \\ &\quad = 4\pi e^2([k]\,[k'])^{-1/2} \sum_{SS'} q_S q_{S'} G^{(SS')}_{km,k'm'}\,(t), \end{aligned} \qquad (6)$$

where q_S is the effective charge of sth ligand. The result of the calculation of correlation function $G^{(SS')}_{km,k'm'}(t)$ is given by Eqs. (A.1)–(A.3) in the appendix. Substituting Eq. (5) in Eqs. (1)–(3) gives the expression for probabilities of vibronically induced forced electric dipole transitions in the framework of the point charge model. However, the obtained expression is too cumbersome. By applying the Judd–Ofelt method [1,8] for the calculation of probabilities intermultiplet transitions, one finds that the averaged probability $\bar{W}$ of photon absorption accompanied by absorption or emission of phonons is given by

$$\bar{W} = (2\pi\chi\alpha P/3\hbar\,[J][J']) \times \int_{-\infty}^{\infty} \exp\,[\mathrm{i}(\Delta - \Omega)t] S_{JJ'}(t)\,\mathrm{d}t, \tag{7}$$

where

$$S_{JJ'}(t) \equiv \sum_{q,MM'} \langle d_q(t) d_{-q}(0)\rangle = \sum_{km\lambda} [\lambda](J\|U^{(\lambda)}\|J')^2 \times \langle A_{km}(t) A^*_{km}(0)\rangle \Xi^2(k,\lambda)/[k]. \tag{8}$$

It should be noted that $S_{JJ'}(0)$ is the usual expression for the zero phonon line (ZPL) strength of $J \to J'$ intermultiplet transition. Hence, Eq. (7) can be rewritten as

$$\bar{W} = (2\pi\chi\alpha P/3\hbar[J][J']) \sum_{n=1} \Omega^{(n)}_{\lambda}(J\|U^{(\lambda)}\|J'), \tag{9}$$

where

$$\Omega^{(n)}_{\lambda} = [\lambda] \sum_{kSS'} 4\pi e^2 q_S q_{S'} \Xi^2(k,\lambda) \times T^{SS'}_{k}(n) J^{(n)}_{SS'}(\Delta - \Omega)/[k]^2. \tag{10}$$

In Eq. (10) $T^{SS'}_k(n)$ is given in the appendix, and the spectral density is given by

$$J^{(n)}_{SS'}(\omega) = \int_{-\infty}^{\infty} \mathrm{e}^{\mathrm{i}\omega t} K^n_{SS'}(t)\,\mathrm{d}t. \tag{11}$$

In Eqs. (9)–(11) n is the number of phonons involved in the intermultiplet transition. Eq. (9) is precisely of the same form as Eq. (16) [1]. The expression (10) for $\Omega^{(n)}_{\lambda}$ can be simplified by using the approximation of the additive contributions of the ligands motion to the sideband intensities (when $K_{SS'}(t) = K(t)\delta_{SS'}$):

$$\Omega^{(n)}_{\lambda} = Z e^2 q^2_{\mathrm{L}} \sum_{k} \frac{(2n+2k)!\,[\lambda]}{[k]!\,n!\,2^n R^{2(k+1)}} \times \Xi^2(k,\lambda) J^{(n)}(\Delta - \Omega), \tag{12}$$

where Z is the number of anions nearest to the RE ions, R is the equilibrium distance between RE ion and ligand, q_{L} is the effective charge of ligand.

Finally, in a single-frequency (ω_0) model of crystal vibrations we obtain

$$\Omega^{(n)}_{\lambda} = \frac{2\pi Z e^4 q^2_{\mathrm{L}}}{\omega_0} \sum_{k} \frac{(2n+2k)!\,[\lambda]}{[k]!\,n!\,R^{2(k+1)}} \times \Xi^2(k,\lambda)\eta^n \Theta_n, \tag{13}$$

where $\Theta_n = \langle N+1\rangle^n$ and $\langle N\rangle^n$ for Stokes and anti-Stokes absorption band, respectively ($\langle N\rangle = [\exp(\hbar\omega_0/kT) - 1]^{-1}$ is a mean phonon-occupation number). The quantity $\eta = \langle u^2\rangle/R^2$ in Eq. (13) is the parameter characterizing dynamical properties of lattice [5–7]. The value of $\langle u^2\rangle$ can be roughly estimated as $\hbar/2M\omega_0$, where M is a reduced mass of ions involved, mainly ligands. Hence, values of η are expected in the region 10^{-3}–10^{-4}. In Ref. [1] quantity Ξ includes a 3j, 6j-symbols and sum $\sum(nl\,|\,r\,|\,n'l')\,(nl\,|\,r^k\,|\,n'l')/\Delta(n'l')$. This sum was calculated for a number of RE ions in Refs. [9,10]. So, the $\Omega^{(n)}_{\lambda}$ parameter can be easily estimated by using Eq. (13).

3. Non-Coulomb interaction contribution to multiphonon sideband

As noted above, the non-Coulomb part of crystal field is described by the Hamiltonian H_{E} (see Eq. (4)). In this case [4]

$$d_q = \sum_{jkm\lambda} [\lambda](-1)^{m+q} \begin{pmatrix} 1 & \lambda & k \\ q & -m-q & m \end{pmatrix} \times (i\,|U^{(\lambda)}_{m+q}|\,f)_{4\mathrm{f}} A_{km}(\boldsymbol{r}_j)\,\Xi\,(j,k\,;\lambda), \tag{14}$$

where

$$A_{km}(\boldsymbol{r}_j) = ([k]/4\pi)^{1/2} Y^*_{km}(\boldsymbol{r}_j),$$

$$\times\,\Xi\,(j,k\,;\lambda) = 2\sum\,[l\,][l'\,]\,(-1)^{l+l'} \begin{Bmatrix} 1 & \lambda & k \\ l & l' & l \end{Bmatrix} \times \begin{pmatrix} l & 1 & l' \\ 0 & 0 & 0 \end{pmatrix} \cdot \begin{pmatrix} l' & k & l \\ 0 & 0 & 0 \end{pmatrix} \times (nl\,|\,\xi\,|\,n'l')(n'l'\,|\,B_k(r_j)\,|\,nl)/\Delta(n'l'), \tag{15}$$

$$(n'l' \mid B_k(r_j)| \, nl) = \{8\pi e^2/r_j\,([l\,][l'])^{1/2}\}G(nl, n'l')$$
$$\times [S_s(j, nl)S_s(j, n'l') + S_\sigma(j, nl)\, S_\sigma(j, n'l')$$
$$+ \gamma_k(ll')\, S_\pi(j, nl)S_\pi(j, n'l')]. \qquad (16)$$

Here $G(nl, n'l')$ are dimensionless fitting parameters (which, in particular, determine ZPL intensity), $\gamma_k(ll') = [l(l+1) + l'(l'+1) - k(k+1)]/[l(l+1)l'(l'+1)]^{1/2}$, and $S_\nu(j, nl)$ ($\nu = s, \sigma, \pi$) denotes the overlap integral of the nl-configuration electron wave function of RE ion with the wave function of the external electron shell in jth ligand. In the important case of RE ions surrounded by oxygen or fluorine ions, these ligand wave functions are of $2p\sigma$, $2p\pi$, and $2s$ type. A general expression for $\langle d_q(t)d_{q'}(0)\rangle$ is too cumbersome. Here we give only an expression for $S_{JJ'}(t)$ in the approximation of additive contributions of ligands to multiphonon sidebands. In this case

$$S_{JJ'}(t) = \frac{Z}{4\pi^2}\sum_{km\lambda}[\lambda]\langle\, \Xi(k, \lambda; t)\, \Xi(k, \lambda)\rangle, \qquad (17)$$

$$\Xi(k, \lambda; t)$$
$$= \exp(\mathrm{i}H_{\mathrm{L}}t/\hbar)\, \Xi(k, \lambda)\exp(-\mathrm{i}H_{\mathrm{L}}t/\hbar). \qquad (18)$$

The quantity $\Xi(k, \lambda)$ in Eqs. (17) and (18) can be written as

$$\Xi(k, \lambda) = \sum_\mu C_\mu(k\lambda)\rho_\mu(r), \qquad (19)$$

where $\rho_\mu(r) = \exp(-\alpha_\mu r)/r$. Here we take into account that to good approximation the overlap integrals $S_s(nl)$, $S_s(n'l')$ in Eq. (16) can be represented in the form $S_0\exp(-\gamma r)$. Coefficients $C_\mu(k\lambda)$ can be found from Eqs. (15) and (16). Hence, we have

$$\langle\, \Xi(k, \lambda; t)\, \Xi(k, \lambda)\rangle$$
$$= \sum_{\mu\mu'} C_\mu(k\lambda)C_{\mu'}(k\lambda)F_{\mu\mu'}(t), \qquad (20)$$

where the expression for the correlation function $F_{\mu\mu'}(t)$ is given by Eqs. (A.5) and (A.6). In the case considered, the modulation of the RE ion–ligand distance r results in the modulation of the overlap integrals, which, in turn, contribute to the multiphonon sideband. In a single-frequency model for crystal vibrations we obtain

$$\Omega^{(n)}_\lambda = \frac{Z}{2\pi\omega_0}\sum_{\mu\mu'} C_\mu(k\lambda)C_{\mu'}(k\lambda)\, \Phi_{\mu\mu'}(n)\, \eta^n. \qquad (21)$$

The expression for $\Phi_{\mu\mu'}(n)$ follows from Eq. (A.6) in appendix.

4. Discussion

The M-process implies that lattice Hamiltonian does not change during $|\,i\,) \to |\,f\,)$ transition. On the contrary, the Δ-process is essentially caused by the change (shifts of equilibrium position of ions and/or change in lattice frequencies) in lattice state under $|\,i\,) \to |\,f\,)$ transition [11]. The theory of both processes has a common problem related to the mathematical difficulties of phonon factor calculation, namely, the spectral density $J^{(n)}(\omega)$ and Huang–Rhys parameter S. At present, it is not clear which process will dominate. To our knowledge the only experimental paper on multiphonon sidebands in RE ions is the paper [12]. Further experimental and theoretical studies are necessary for a detailed description of phonon sidebands formation.

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Appendix A

A.1. The correlation functions in the harmonic approximation

$$G^{(SS')}_{km,k'm'} = \langle \exp(\mathrm{i}H_{\mathrm{L}}t/\hbar)\,(Y^*_{km}(\boldsymbol{r}_S)/r_S^{k+1})$$
$$\times \exp(-\mathrm{i}H_{\mathrm{L}}t/\hbar)\,(Y^*_{k'm'}(\boldsymbol{r}_{S'})/r_{S'}^{k'+1})\rangle$$
$$= \sum_{n=0}^{\infty} T^{(SS')}_{km,k'm'}(n)\, K^n_{SS'}(t), \qquad (\mathrm{A}.1)$$

where

$$T^{(SS')}_{km,k'm'}(n) = \frac{(-1)^{k+k'}\cdot\{[k][k'](2n+2k)!(2n+2k')!/(2k)!(2k')!\}^{1/2}}{R_S^{k+1}R_{S'}^{k'+1}2^n n!}$$
$$\times \sum_p (-1)^{m+m'} \begin{pmatrix} n+k & n & k \\ -p-m & p & m \end{pmatrix} \times \begin{pmatrix} n+k' & n & k' \\ -p-m' & p & m' \end{pmatrix} \cdot Y^*_{n+k,p+m}(\boldsymbol{n}_{S0}) \cdot Y_{n+k',p+m'}(\boldsymbol{n}_{S'0}) \qquad \text{(A.2)}$$

and

$$K_{SS'}(t) = \langle \boldsymbol{u}_S(t)\boldsymbol{u}_{S'}\rangle / 3R_S R_{S'}. \qquad \text{(A.3)}$$

$$T^{(SS')}_k = \sum_m T^{(SS')}_{km,km}(n) = \frac{[k]}{4\pi}\cdot\frac{(2n+2k)!}{(2k)!n!2^n(R_S R_{S'})^{k+1}} P_{n+k}(\boldsymbol{n}_{S0}\boldsymbol{n}_{S'0}), \qquad \text{(A.4)}$$

where $P_{n+k}(\boldsymbol{n}_{S0}\boldsymbol{n}_{S'0})$ is the Legendre polynomial. (In Eqs. (A.1)–(A.4) $\boldsymbol{r}_S = \boldsymbol{R}_S + \boldsymbol{u}_S$, R_S is equilibrium distance between RE ion and sth ligand, $\boldsymbol{n}_{S0} = \boldsymbol{R}_S/R_S$).

$$F^{(SS')}_{\mu\mu'}(n) = \langle \exp(\mathrm{i}H_{\mathrm{L}}t/\hbar)\,[\exp(-\alpha_\mu r_S)/r_S] \times \exp(-\mathrm{i}H_{\mathrm{L}}t/\hbar)\,[\exp(-\alpha_{\mu'} r_{S'})/r_{S'}]\rangle = \sum_{n=1} \Phi^{(SS')}_{\mu\mu'}(n)[K_{SS'}(t)/2]^n, \qquad \text{(A.5)}$$

where

$$\Phi^{(SS')}_{\mu\mu'}(n) = \rho_\mu(R_S)\rho_{\mu'}(R_{S'})\pi^{-1/2}(\tau_{S\mu}\tau_{S'\mu'})^{n+1/2} \times \exp(\tau_{S\mu}+\tau_{S'\mu'}) \sum_{p=0}^{\mathrm{Int}(n/2)} \frac{(2n-4p+1)P_{n-2p}(\boldsymbol{n}_{S0}\boldsymbol{n}_{S'0})}{\Gamma(p+1)\Gamma(n-p+3/2)} \times K_{n-2p+1/2}(\tau_{S\mu})K_{n-2p+1/2}(\tau_{S'\mu'}) \qquad \text{(A.6)}$$

$\tau_{S\mu} = \alpha_\mu R_S$, Int$(n/2)$ is the integer part of $n/2$, $\Gamma(x)$ is a gamma function, and $K_{n-2p+1/2}(x)$ is a MacDonald function.

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