

# Phonon Sidebands, Multiphonon Relaxation of Excited States, and Phonon-Assisted Energy Transfer between Ions in Solids\*

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A unified treatment is given in the adiabatic approximation for phonon sideband intensities, multiphonon relaxation transition probabilities, and phonon-assisted energy-transfer probabilities. The intensity distribution of phonon sidebands is determined by coupling constants of the vibrational modes with electrons or holes and a criterion for the appearance of discrete sidebands is given. Transition probabilities of multiphonon relaxation processes among various excited levels of an ion are shown to depend exponentially on the energy gap between these levels, in agreement with recent experimental results. A similar dependence is derived for the energy-transfer probabilities between two ions on the energy mismatch between excitation energies of these ions.

## 1. INTRODUCTION

DISCOVERY of laser action in various hosts containing transition ions and rare-earth ions has stimulated studies of optical spectra, relaxation processes, and energy-transfer processes between pairs of ions in these systems, and detailed information regarding these processes is being accumulated.<sup>1,2</sup>

It is well known that phonons play an important role in these processes. In fact, one can infer the phonon density of states from the multiphonon structure of absorption or emission spectra, and often the cutoff frequency of the phonon spectra is deduced from this kind of observation.<sup>1,3</sup> When the coupling between lattice modes and the electron (or hole) in question is sufficiently strong the multiphonon structure is smoothed out and only a single broad (Gaussian-like) band is obtained, whereas multiphonon structure is visible for weak or intermediate coupling.<sup>4,5</sup> However, there seems to be no clear criterion stated in the literature to discriminate between these two limiting cases, nor do there seem to be theoretical expressions which are useful in the analysis of observed spectra in which multiphonon structure is superimposed on the broad background absorption or emission band.

Furthermore, experimental results and subsequent analysis on the relaxation times between various excited levels of rare-earth (RE) ions<sup>6,7</sup> suggest that

these relaxation processes occur through multiphonon emission. From the analysis the relaxation rates are found to depend exponentially on the energy gap between levels involved in the process. Also it is a well-known empirical fact that fluorescence from a level will only be seen if a lower-lying level is separated from the first by an energy which exceeds some critical value.<sup>8</sup> These facts should be explicable by the interaction with the phonons which are responsible for the phonon sidebands. Kiel<sup>9</sup> has developed a perturbational expansion for  $n$ -phonon processes but the results cannot be placed in closed form.

Finally, the same multiphonon processes should be involved in the energy-transfer process between ions in which excitation energies of the two ions have a large mismatch in the absence of vibrational transition. Orbach<sup>10</sup> has formulated a theory for two-phonon processes in ruby.

During an analysis<sup>11</sup> of sensitized luminescence of weakly coupled  $RE^{3+} + Yb^{3+}$  systems in various hosts it became necessary to estimate the probability of energy transfer between ions in which the energy mismatch of excitation energies sometimes amounts to  $2000\text{ cm}^{-1}$ , many times a phonon energy. Although the standard formal expressions<sup>12</sup> for transfer probability are applicable, it was not possible to evaluate the density of phonon states from overlap integrals of measured absorption and emission spectra in the usual way, but from measured relaxation rates and the following theory it was possible to make reasonable estimates. In the present paper we describe a theory for the three multiphonon processes mentioned above, assuming a simplified model which we hope represents the essential aspects of the problems. In the next sec-

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<sup>1</sup> W. M. Yen, W. C. Scott, and A. L. Shawlow, *Phys. Rev.* **136**, A271 (1964).

<sup>2</sup> See, for instance, *Optical Properties of Ions in Crystals*, edited by H. M. Crosswhite and H. W. Moos (Wiley-Interscience, Inc., New York, 1967), and references cited therein.

<sup>3</sup> I. Richman, *Phys. Rev.* **133**, A1364 (1964); E. Cohen and H. J. Guggenheim, *Bull. Am. Phys. Soc.* **13**, 88 (1968).

<sup>4</sup> M. Wagner, *J. Chem. Phys.* **41**, 3939 (1964).

<sup>5</sup> Y. Toyozawa, in *Dynamical Processes in Solid State Optics*, edited by R. Kubo and H. Kamimura (W. A. Benjamin, Inc., New York, 1967), p. 90.

<sup>6</sup> M. J. Weber, in Ref. 2, p. 473; M. J. Weber, *Phys. Rev.* **156**, 231 (1967); **157**, 262 (1967); **171**, 283 (1968).

<sup>7</sup> L. A. Riseberg, W. A. Gandrud, and H. W. Moos, *Phys. Rev.* **159**, 262 (1967); L. A. Riseberg and H. W. Moos, *ibid.* **174**, 429 (1968).

<sup>8</sup> See, for instance, M. J. Weber, Ref. 6.

<sup>9</sup> A. Kiel, in *Quantum Electronics*, edited by P. Grivet and N. Bloembergen (Columbia University Press, New York, 1964), Vol. 1, p. 765.

<sup>10</sup> R. Orbach, in Ref. 2, p. 445.

<sup>11</sup> T. Miyakawa and D. L. Dexter, *Phys. Rev.* (to be published).

<sup>12</sup> Th. Förster, *Ann. Physik* **2**, 55 (1948); D. L. Dexter, *J. Chem. Phys.* **21**, 836 (1953).

tion we explain our model and approximations; the method of generating functions first developed by Kubo,<sup>13</sup> Kubo and Toyozawa,<sup>14</sup> and Lax<sup>15</sup> will be reviewed in Sec. 3; in Sec. 4, we derive and discuss the formulas for the phonon sideband intensity distribution; the gap and temperature dependence of the multiphonon relaxation rates are derived and discussed in Sec. 5; Sec. 6 is devoted to the derivation and discussion of the formula for the phonon-assisted energy-transfer probability. The results are summarized and discussed in the final section. Throughout we shall have RE systems particularly in mind, although many of our results are not restricted to these materials.

## 2. MODEL AND APPROXIMATIONS

In this paper we restrict ourselves, depending on the phenomenon under discussion, to cases in which there are either one or two ions of interest in the system. In considering energy transfer between two ions, we assume that the interaction between them is so weak that we may ignore it as regards the shape of the absorption and emission spectra and the nonradiative intraion relaxation probability. As the overlap between  $4f$  wave functions on different RE ions in which we are most interested is extremely small,<sup>11</sup> we may safely neglect the effect of exchange and overlap in our treatment of these two ions, and thus may treat them in the Hartree approximation.

Denoting the coordinates of electrons (or holes) of the ions and the lattice by  $r$  and  $Q$ , respectively, we can write down the total Hamiltonian of the system as

$$H_T = H(\mathbf{r}, \mathbf{Q}) + H_R + H_{eR}, \quad (2.1)$$

$$H(\mathbf{r}, \mathbf{Q}) = H_e(\mathbf{r}) + H_L(\mathbf{Q}) + H_{eL}(\mathbf{r}, \mathbf{Q}), \quad (2.2)$$

where  $H_e$ ,  $H_L$ ,  $H_{eL}$ ,  $H_R$ , and  $H_{eR}$  are the energy of electrons, the lattice vibrations, the interaction energy between electrons and lattice, the energy of the radiation field, and the interaction between electrons and the radiation field, respectively. More specifically, the electronic energy consists of two parts,

$$\begin{aligned} H_e(\mathbf{r}) &= H^0(\mathbf{r}_1, \mathbf{r}_2) + H_{ab}(\mathbf{r}_1, \mathbf{r}_2) \\ &= H_a(\mathbf{r}_1) + H_b(\mathbf{r}_2) + H_{ab}(\mathbf{r}_1, \mathbf{r}_2). \end{aligned} \quad (2.3)$$

Here  $H_a(\mathbf{r}_1)$  and  $H_b(\mathbf{r}_2)$  denote the Hamiltonians of the sets of electrons 1 and 2 localized, respectively, around ions  $a$  and  $b$  and  $H_{ab}(\mathbf{r}_1, \mathbf{r}_2)$  is the interaction between electrons 1 on ion  $a$  and electrons 2 on ion  $b$ .

As we are assuming that the interaction  $H_{ab}(\mathbf{r}_1, \mathbf{r}_2)$  is weak, and that electrons are well localized around ions  $a$  and  $b$ , we may use the adiabatic approximation in dealing with the lattice vibrations. We first solve for the eigenvalues and eigenfunctions of electrons for fixed lattice coordinates  $Q$ ,

$$[H^0(\mathbf{r}) + H_{eL}(\mathbf{r}, \mathbf{Q})]\Phi_j(\mathbf{r}, \mathbf{Q}) = W_j(\mathbf{Q})\Phi_j(\mathbf{r}, \mathbf{Q}), \quad (2.4)$$

<sup>13</sup> R. Kubo, Phys. Rev. **86**, 929 (1952).

<sup>14</sup> R. Kubo and Y. Toyozawa, Progr. Theoret. Phys. (Kyoto) **13**, 162 (1955).

<sup>15</sup> M. Lax, J. Chem. Phys. **20**, 1752 (1952).

and then use this  $Q$ -dependent eigenvalue  $W_j(Q)$  as the state-dependent potential for the lattice vibrations,

$$[H_L(\mathbf{Q}) + W_j(\mathbf{Q})]X_{jv}(\mathbf{Q}) \equiv H_{jv}X_{jv} = E_{jv}X_{jv}(\mathbf{Q}). \quad (2.5)$$

In this approximation we can write the wave function of the total atomic system in the following form:

$$\Psi_{jv}(\mathbf{r}, \mathbf{Q}) = \Phi_j(\mathbf{r}, \mathbf{Q})X_{jv}(\mathbf{Q}), \quad (2.6)$$

$$\Phi_j(\mathbf{r}, Q) = \varphi_{j_a}(\mathbf{r}_1, Q)\varphi_{j_b}(\mathbf{r}_2, Q), \quad (2.7)$$

where  $j_a$ ,  $j_b$  specify the electronic states of  $a$  and  $b$  ions.

It is to be noted that the zero-order eigenfunction (2.6) is not strictly a stationary state of the system because of the  $Q$  dependence of the electronic wave functions. Indeed, the nonadiabatic part of the Hamiltonian  $H_{NA}$  defined by

$$\begin{aligned} H_{NA}\Psi_{jv}(\mathbf{r}, Q) &\equiv (H - E_{jv})\Psi_{jv}(\mathbf{r}, Q) \\ &= H_L(\Phi_{jv}X_{jv})\Phi_j(H_LX_{jv}) \end{aligned} \quad (2.8)$$

acts as the effective interaction which causes non-radiative transitions between levels of an ion.

Contrary to an earlier statement,<sup>9</sup> a small Stokes's shift does not in itself imply breakdown of the adiabatic approximation. The adiabatic approximation can be applied for systems with discrete levels in which coupling through electron-photon, interion, or nonadiabatic parts of the Hamiltonian is weak compared with that through  $H_{eL}$ . Furthermore, as we shall see in the following, it provides the most natural systematic starting point to include higher-order effects when combined with the method of generating functions.

In this respect it should be noted that in principle one need not restrict oneself to a linear or quadratic form of  $H_{eL}(\mathbf{r}, Q)$  provided the trace of certain operators can be evaluated in a reasonable approximation. All one needs usually is to assume that it is possible to approximate the adiabatic potential  $U_j$ , the sum of the state-dependent effective potential  $W_j(Q)$  and the lattice potential by harmonic potentials with different equilibrium positions and possibly with different frequencies. However, we restrict ourselves here to the case of a linear interaction. The higher-order terms in the interaction Hamiltonian will cause higher-order effects such as asymmetry in the intensity distribution of absorption and emission lines or nonequidistant structure of the phonon sidebands. As we have, so far, almost no information regarding these higher-order effects, we may assume that these effects are not very important. Moreover, the inclusion of these terms will not alter, at least qualitatively, the main conclusions in this paper, i.e., the exponential dependence on the energy difference of the relative intensity distribution of phonon sidebands, of the relaxation rate, and of the phonon-assisted energy-transfer probability.

Thus we assume a general linear interaction Hamiltonian

$$H_{eL}(\mathbf{r}, \mathbf{Q}) = -\sum_s V_s(\mathbf{r})Q_s, \quad (2.9)$$

summing over all lattice normal modes.

Even when we restrict ourselves to the linear term in  $H_{eL}$  we still have higher-order effects in the adiabatic potential which come from higher-order contributions of  $H_{eL}$  to  $W_j(Q)$ . These effects will also be neglected in the following for the same reason as above. Thus we use the lowest-order approximation for the wave functions  $\Phi_j(\mathbf{r}, \mathbf{Q})$  and adiabatic potential  $U_j(Q)$ ,

$$\Phi_j(\mathbf{r}, \mathbf{Q}) = \Phi_j^{(0)}(\mathbf{r}) - \sum_{s, k \neq j} \frac{V_{sjk} \Phi_k^{(0)}(\mathbf{r}) Q_s}{(\mathcal{E}_j^{(0)} - \mathcal{E}_k^{(0)})}, \quad (2.10)$$

$$U_j(\mathbf{Q}) = \mathcal{E}_j^{(0)} + \frac{1}{2} \sum_s \omega_s^2 Q_s^2 + \sum_s V_{sjj} Q_s - \sum_{s, s' k \neq j} \frac{V_{sjk} V_{s'kj} Q_s Q_{s'}}{(\mathcal{E}_j^{(0)} - \mathcal{E}_k^{(0)})}, \quad (2.11)$$

where  $\mathcal{E}_j^{(0)}$  is the zero-order energy of the  $j$ th electronic state and

$$V_{sjk} \equiv \int \Phi_j^{(0)}(\mathbf{r}) V_s(\mathbf{r}) \Phi_k^{(0)}(\mathbf{r}) d\mathbf{r}. \quad (2.12)$$

The superscript (0) means that the quantity is evaluated at the equilibrium positions of the lattice coordinates for that state. We have assumed that the lattice potential in the ground electronic state is already diagonalized by the introduction of the lattice normal modes  $Q_s$  [i.e., we assume that for the ground state the third and fourth terms in (2.11) vanish].

We may neglect the last term in (2.11) in the following because we have no evidence for a lattice frequency shift in the optical spectra of RE ions. In this approximation we have

$$U_k(\mathbf{Q}) = \mathcal{E}_k + \frac{1}{2} \sum_s \omega_s^2 [Q_s - Q_s(k)]^2, \quad (2.13)$$

$$\mathcal{E}_k = \mathcal{E}_k^{(0)} - \frac{1}{2} \sum_s (V_{skk}/\omega_s)^2, \quad (2.14)$$

$$Q_s(k) = V_{skk}/\omega_s^2, \quad (2.15)$$

the last expression being the shift in equilibrium lattice coordinates in the final state.

Also the nonadiabatic part of the Hamiltonian  $H_{NA}$  defined through (2.8) can be given to the lowest order by

$$(H_{NA})_{kj} = -i \sum_s S_{skj} \frac{\partial}{\partial Q_s}, \quad (2.16)$$

$$S_{skj} = -i\hbar^2 \int \Phi_k^*(\mathbf{r}, Q) \frac{\partial \Phi_j(\mathbf{r}, Q)}{\partial Q_s} d\mathbf{r} = -i\hbar^2 V_{skj} / (\mathcal{E}_j^{(0)} - \mathcal{E}_k^{(0)}). \quad (2.17)$$

For the interionic interaction  $H_{ab}(r_1, r_2)$  we may use a multipole expansion because we are assuming a large separation  $R_{ab}$  between ions  $a$  and  $b$ . In the case of  $4f$  electrons in RE ions the quadrupole-quadrupole interaction will be dominant<sup>10</sup>:

$$H_{ab}(r_1, r_2) = 4\pi e^2 r_1^2 r_2^2 / 5R_{ab}^5 \times \sum_{m=-2}^2 C_m V_{2m}(\theta_1, \phi_1) Y_{2-m}(\theta_2, \phi_2),$$

$$C_0 = 1, \quad C_1 = C_{-1} = -4, \quad C_2 = C_{-2} = 1. \quad (2.18)$$

In the case of energy transfer we must be careful in evaluating matrix elements of  $V_s(\mathbf{r})$ . As we are dealing here with a two-electron system instead of just one as in the phonon sideband and multiphonon relaxation cases,  $V_{skj}$  becomes

$$V_{skj} = V_{ska} j_a + V_{skb} j_b. \quad (2.12')$$

Assuming that the zero-order wave functions (2.6) and (2.7) are known, our threefold problem is to find the transition probabilities between various levels caused either by (a)  $H_{eR}$ , i.e., by absorption or emission of a photon or by (b)  $H_{NA}$ , i.e., by a nonradiative relaxation process; and (c) to find the probability of energy transfer between ions  $a$  and  $b$  through  $H_{ab}$ . Only ion  $a$  will be considered in cases (a) and (b).

Formulated in this way it is clear that the three problems can be handled by a single technique (with minor modifications) which leads, at least formally, to closely related results.

Finally, it should be remarked that we make the usual important assumption that the initial phonon state is in thermal equilibrium with the surroundings and can be characterized by a Boltzmann distribution

$$W_i = e^{-\beta E_{jv}} / \text{Tr} \rho_j(\beta), \quad \beta = 1/k_B T^*, \quad (2.19)$$

with an effective temperature  $T^*$ . Here  $\rho_j(\lambda)$  is the density matrix for the vibrational states

$$\rho_j(\lambda) = \sum_v e^{-\lambda E_{jv}} P(x_{jv}), \quad (2.20)$$

and  $P(X_{jv})$  is the projection operator onto the state  $X_{jv}$ .

In the case of optical absorption this is not an assumption but simply a definition of the ground state, with  $T^* = T$ . For other cases which involve excited electronic states there may be cases in which this assumption is not valid. For the electrons in RE ions, however, which have fairly long decay times (up to 10 msec) in various excited states this assumption may be justified with  $T^*$  closely equal to the lattice temperature.

### 3. METHOD OF GENERATING FUNCTIONS

The necessary formalism is already worked out<sup>14</sup> and rather detailed analyses of phonon side bands were given by Wagner<sup>4</sup> and by Toyozawa.<sup>5</sup> Kubo and Toyozawa<sup>14</sup> also gave an expression for the nonradiative transition probability but they were concerned only with the strong-coupling limit and no analysis was made of the multiphonon relaxation at that time. The expression for the phonon-assisted energy transfer, Eq. (6.16), is to our knowledge derived here for the first time.

We start from the observation that in a crystal containing  $N_a$  ions the optical-absorption constant  $A(\nu)$ , the nonradiative transition probability per unit time  $W_{NA}$ , and the energy-transfer probability per unit time between ions  $a$  and  $b$ ,  $W_{ab}$ , can be written in terms of spectral functions  $F_Z(E)$  of some operator  $Z$ . Thus

$$A(\nu) = (8\pi^3 N_a / 3nc) \nu F_M(h\nu), \quad (3.1)$$

$$W_{NA} = 2\pi / \hbar F_{NA}(0), \quad (3.2)$$

$$W_{ab} = 2\pi / \hbar F_{ab}(0), \quad (3.3)$$

where

$$F_Z(E) \equiv \sum_{v, v'} |\langle f | Z | i \rangle|^2 W_i \delta(E - E_f + E_i). \quad (3.4)$$

Here  $c$  and  $n$  are the velocity of light in vacuum and the index of refraction of the crystal, respectively, and we have omitted any local field correction factor in (3.1) for simplicity. In (3.4),  $f$  and  $i$  label the final ( $kv'$ ) and the initial ( $kv$ ) states, and  $W_i$  is defined in (2.19).

The operator  $Z$  in Eq. (3.4) can be  $\mathbf{M} = e\mathbf{r}$ , i.e., the dipole moment operator<sup>16</sup> for the optical absorption,  $H_{NA}$  given by (2.16) for nonradiative relaxation, or  $H_{ab}$  given by (2.18) for the case of energy transfer. Thus the three problems reduce to the evaluation of the spectral function  $F_Z(E)$  in each case.

The spectral function  $F_Z(E)$  can be calculated from the generating function  $f_Z(\lambda)$  defined as the Laplace transform of  $F_Z(E)$ ,

$$f_Z(\lambda) = \int_{-\infty}^{\infty} F_Z(E) e^{-\lambda E} dE, \quad (3.5)$$

which in turn can be calculated in the form of a trace of products of  $Z$  and the density matrices  $\rho_j(\lambda)$ ,

$$f_Z(\lambda) = \text{tr}[Z_{jk} \rho_k(\lambda) Z_{kj} \rho_j(\beta - \lambda)] / \text{tr} \rho_j(\beta), \quad (3.6)$$

where  $Z_{jk}$  is the matrix element of  $Z$  between electronic wave functions  $\Phi_j^{(0)}$  and  $\Phi_k^{(0)}$  and may still be an operator as regards the lattice coordinates,

$$Z_{jk} \equiv \int \Phi_j^{(0)*}(\mathbf{r}) Z(\mathbf{r}, Q) \Phi_k^{(0)}(\mathbf{r}) d\mathbf{r}. \quad (3.7)$$

It is given by (2.16) for the case of nonradiative relaxation. In the cases of optical absorption and of energy transfer we have in the lowest approximation

$$M_{kj}(Q) = M_{kj}^{(0)} + \sum_s (M_{kj}^{(1)})_s Q_s, \quad (3.8)$$

$$(M_{kj}^{(1)})_s = \sum_{\kappa \neq k, j} \left( \frac{M_{k\kappa}^{(0)} V_{s\kappa j}}{\mathcal{E}_j^{(0)} - \mathcal{E}_\kappa^{(0)}} + \frac{V_{s\kappa k} M_{\kappa j}^{(0)}}{\mathcal{E}_\kappa^{(0)} - \mathcal{E}_k^{(0)}} \right), \quad (3.9)$$

$$(H_{ab})_{kj}(Q) = (H_{ab})_{kj}^{(0)} + \sum_s (H_{ab}^{(1)})_{kjs} Q_s, \quad (3.10)$$

<sup>16</sup>  $Z$  will be the quadrupole operator for E. Q. or the magnetic dipole operator for M. D. transitions.

$$(H_{ab}^{(1)})_{kjs} = \sum_{\kappa \neq k, j} \left( \frac{(H_{ab})_{k\kappa}^{(0)} V_{s\kappa j}}{\mathcal{E}_j^{(0)} - \mathcal{E}_\kappa^{(0)}} + \frac{V_{s\kappa k} (H_{ab})_{\kappa j}^{(0)}}{\mathcal{E}_\kappa^{(0)} - \mathcal{E}_k^{(0)}} \right). \quad (3.11)$$

Since  $M$  and  $H_{ab}$  have the same dependence on lattice coordinates  $Q_s$  in this approximation, we can use the results of Kubo and Toyozawa for  $H_{ab}$  as well. We merely have to rederive their formulas for the case of weak or intermediate coupling.

The  $Q$  dependence of  $H_{ab}$  will not be important in most cases, whereas the dependence of  $M_{kj}$  [Eq. (3.8)] on  $Q$  is responsible for the vibration-induced transitions. This effect may be taken into account if we replace  $|M^{(0)}|^2$  in the following equations by  $|M^{(1)}|^2 \times (\hbar/2\omega) \coth(\frac{1}{2}\beta\hbar\omega)$ .<sup>17</sup>

In this approximation the generating functions discussed in Ref. 14 are given by

$$f_M(t) = f_0(t) |M^{(0)}|^2, \quad (3.12)$$

$$f_{NA}(t) = f_0(t) g_{NA}(t), \quad (3.13)$$

$$f_{ab}(t) = f_0(t) |H_{ab}^{(0)}|^2, \quad (3.14)$$

where, denoting the excitation energy or energy gap  $\mathcal{E}_k^{(0)} - \mathcal{E}_j^{(0)}$  by  $\mathcal{E}_0$ ,

$$f_0(t) = \exp[i\mathcal{E}_0 t / \hbar - g + g_+(t) + g_-(t)] \quad (3.15)$$

is the generating function which determines the optical line shape, with  $g$ ,  $g_\pm^{(\pm)}$  defined by

$$g = g_+(0) + g_-(0) = \int d\omega D(\omega) (2n_\omega + 1), \quad (3.16)$$

$$g_\pm(t) = \int d\omega D(\omega) \left\{ \begin{matrix} n_\omega \\ n_\omega + 1 \end{matrix} \right\} \exp(\pm i\omega t), \quad (3.17)$$

in which

$$D(\omega) \equiv \sum_s (\omega_s \Delta_s^2 / 2\hbar) \delta(\omega - \omega_s) \quad (3.18)$$

is the so-called spectral density of electron-phonon coupling which specifies the strength and the spectral distribution of the electron-phonon coupling. The shift in equilibrium positions of the lattice normal coordinates is given by

$$\Delta_s = Q_s(kk) - Q_s(jj). \quad (3.19)$$

The number of phonons excited at temperature  $T$  is

$$n_\omega(T) = [\exp(\beta\hbar\omega) - 1]^{-1}. \quad (3.20)$$

In Eq. (3.13) we require the nonadiabatic operator  $g_{NA}$  characterizing the strength and the spectral distribution of nonadiabatic coupling

$$g_{NA}(t) = |R - R_+(t) - R_-(t)|^2 + J_+(t) + J_-(t), \quad (3.21)$$

where

$$R = R_+(0) + R_-(0), \quad (3.22)$$

$$R_\pm(t) = \int d\omega L(\omega) \left\{ \begin{matrix} n_\omega \\ n_\omega + 1 \end{matrix} \right\} \exp(\pm i\omega t), \quad (3.23)$$

<sup>17</sup> W. B. Fowler, Phys. Status Solidi (to be published).

$$J_{\pm}(t) = \int d\omega N(\omega) \left\{ \begin{matrix} n_{\omega} \\ n_{\omega}+1 \end{matrix} \right\} \exp(\pm i\omega t), \quad (3.24)$$

$$L(\omega) = \sum_s (\omega_s S_s \Delta_s / 2\hbar) \delta(\omega - \omega_s), \quad (3.25)$$

$$N(\omega) = \sum_s (\omega_s S_s^2 / 2\hbar) \delta(\omega - \omega_s). \quad (3.26)$$

Here, for brevity we have omitted suffices  $kj$  in  $S_{skj}$ , defined by (2.17). We shall use these generating functions and associated definitions in computing the probabilities for optical absorption, nonradiative de-excitation, and energy transfer.

#### 4. BROAD ABSORPTION BAND VERSUS PHONON SIDEBANDS

It is well known in connection with the line shape of  $F$  centers that the generating function (3.12) and (3.15) yields a single broad band under some conditions. It has also been shown<sup>5</sup> that under other conditions the same generating function gives the multiphonon structure. However, the criterion for the existence of the two cases is not yet clear. Toyozawa<sup>5</sup> has argued that in the strong-coupling limit ( $g \gg 5$ ) one has a simple Gaussian line, whereas in the weak- or intermediate-coupling limit ( $g \lesssim 5$ ) multiphonon structure is obtained. While this may be a reasonable criterion, one has to recognize the distinction between conditions for having a single broad band and those for having an approximately Gaussian line shape. The larger the coupling constant  $g$ , the closer is the Poisson distribution  $g^n/n!$  to a Gaussian distribution of intensities, but the condition for the multiphonon components to be resolved is different.

As was noted in Markham's review article,<sup>18</sup> the theory of the line shape of the  $F$  center (or any other localized center with strong coupling to the lattice) proceeds as follows: First, one introduces an *ad hoc* assumption that each "phonon" line has a line shape  $g(\omega)$  which has a width  $\Delta\omega$  larger than the mean phonon frequency  $\bar{\omega}$ . Then one calculates the envelope function for the over-all band shape. Specifically, in the calculation of the generating function one assumes that instead of a possible distribution of phonon frequencies  $\omega_s$  over a range of values of  $\omega$  there is only one (in some cases two) phonon with some mean  $\bar{\omega}$  and replaces the summation

$$g - g_+(t) - g_-(t) = \sum_s \frac{\omega_s \Delta_s^2}{2\hbar}$$

by

$$\left[ \coth\left(\frac{1}{2}\beta\hbar\omega_s\right) - i \sin\omega_s t - \coth\left(\frac{1}{2}\beta\hbar\bar{\omega}\right) \cos\omega_s t \right] \sum_s \frac{\omega_s \Delta_s^2}{2\hbar}.$$

If we make this assumption it is rather straightforward to show that the intensity distribution of

these lines at  $T=0^\circ\text{K}$  can be approximated by

$$F(E) = \frac{|M|^2}{\sqrt{(2\pi\delta^2)}} \exp\left(-\frac{(E - \mathcal{E}_0)^2}{2\delta^2}\right) \sum_{m=0}^{\infty} \delta(E - m\hbar\bar{\omega}), \quad (4.1)$$

with

$$\delta^2 = \int_0^{\infty} (\hbar\omega)^2 D(\omega) (2n_{\omega} + 1) d\omega$$

for  $g > 5$ , and by

$$F(E) = |M|^2 \sum_{m=0}^{\infty} \frac{e^{-g} g^m \delta(E - m\hbar\bar{\omega})}{m!}, \quad (4.2)$$

for  $g \lesssim 5$ . The over-all line shape is given as a convolution of this envelope function and the line-shape function  $g(\omega)$ .

Evidently, the condition for the multiphonon components to be resolved depends on the ratio of the width of the line-shape function  $g(\omega)$ , i.e.,  $\Delta\omega$ , to the mean phonon frequency  $\bar{\omega}$ ,  $r \equiv \Delta\omega/\bar{\omega}$ . If  $r > 1$  we will have a broad band, whereas for  $r < 1$  each phonon component will be resolved. The difficulty is we do not know where the line-shape function comes from.

Work of Wagner<sup>4</sup> has suggested a way to resolve this difficulty. He assumed in the usual way a dipole matrix element which is independent of the lattice coordinates, thus reducing the problem of calculation of the line shape to that of the Franck-Condon factor or the overlap integrals between two harmonic-oscillator eigenfunctions. At low temperatures the absorption line shape is given by the energy dependence, that is, the  $m$  dependence, of

$$I_{0m} = \int X_{j_0}^*(Q) X_{km}(Q) dQ,$$

where  $X_{j_0}$  and  $X_{km}$  are the vibrational wave functions in the ground and excited electronic states. For emission one requires

$$I_{m0} = \int X_{k_0}^*(Q) X_{jm}(Q) dQ.$$

His calculation shows that the generating function for each phonon component can be written as  $g^n/n!$  at  $T=0$  for the case of no lattice frequency shift. This result is just what we would obtain by expanding the generating function (3.15) in power series in  $g_-(t)$  (which is equal to  $g e^{-i\omega t}$  at  $T=0$ ). He then calculated the line shapes of each phonon component, assuming some specific distribution of phonon frequencies. In this way he could show that each phonon component has a line shape which is determined by the spectral density of electron-phonon coupling  $D(\omega)$ . The width of the  $m$ th phonon component increases with  $m$  [for Lorentzian  $D(\omega)$ ] or  $\sqrt{m}$  [for Gaussian  $D(\omega)$ ].

This result suggests an approach in which we first take into account the effect of the spectral density of electron-phonon coupling  $D(\omega)$  and calculate the line-shape function  $G(\omega)$  which is centered around a mean

<sup>18</sup> J. J. Markham, Rev. Mod. Phys. **31**, 956 (1959).

frequency  $\bar{\omega}$  with a width  $\Delta\omega$ . Next we calculate the envelope function or the intensity distribution of these phonon components by the method of generating functions.

The above discussion suggests that the criterion for the resolution of multiphonon components is that the mean frequency of the interacting phonons be larger than the width of the component determined by the spectral density of electron-phonon coupling  $D(\omega)$ .

The mean frequency  $\bar{\omega}$  and the width  $\Delta\omega$  can be expressed in terms of the spectral density of electron-phonon coupling  $D(\omega)$ ,

$$\bar{\omega} = \int \frac{\omega D(\omega) d\omega}{g}, \quad (4.3)$$

$$(\Delta\omega)^2 = \int \frac{\omega^2 D(\omega) d\omega}{g} - \bar{\omega}^2. \quad (4.4)$$

If  $D(\omega)$  can be approximated by a Gaussian

$$D(\omega) = \rho_0 e^{-\eta(\omega-\omega_0)^2}, \quad (4.5)$$

we obtain

$$\bar{\omega} = \omega_0, \quad (4.6)$$

$$(\Delta\omega)^2 = 1/2\eta - \omega_0^2. \quad (4.7)$$

Thus the condition  $r < 1$  reduces to

$$4\eta\omega_0^2 > 1. \quad (4.8)$$

Both  $\omega_0$  and  $\eta$  should be determined mainly by the characteristics of the lattice, but if the center or the electron we are considering is strongly coupled to the lattice, this coupling may introduce localized modes around the center and thus have effects on both of these parameters.

It should be noted, however, that both  $\omega_0$  and  $\eta$  may be relatively independent of the coupling strength characterized by the magnitude of  $g$ . Therefore it should be possible to find a system in which the coupling constant itself is large so that the higher-order multiphonon component has a much larger integrated intensity than that of the zero-phonon component, even though both can still be resolved because  $4\eta\omega_0^2$  remains greater than unity. This seems to be the case in KCl:RE<sup>2+</sup> and AgBr:I.<sup>19</sup> The number of multiphonon components resolved will be, under this criterion, proportional to  $(\bar{\omega}/\Delta\omega)^2$  for a Gaussian  $D(\omega)$  and to  $(\bar{\omega}/\Delta\omega)$  for a Lorentzian  $D(\omega)$ . Furthermore, the shift of lattice frequency will enhance or reduce the number of resolvable components.<sup>20</sup>

As we have seen, there are various aspects of phonon sidebands in the spectra of solids. In one extreme there

are broad unresolved absorption bands (or emission bands) characterized by a large Stokes shift like those of  $F$  band or exciton absorption bands in alkali-halides. In the other extreme belong sharp zero-phonon lines and very weak structure associated with it like that observed in the spectra of RE ions or transition-metal ions in crystals.<sup>21,22</sup> Between these two extremes there are a number of systems like KCl:Sm<sup>2+</sup>,<sup>19</sup> AgBr:I,<sup>23</sup> or  $R'$  centers<sup>24</sup> which exhibit both broad band and sharp multiphonon structure.

According to our discussion in the present section, a broad band or phonon sidebands appear according to whether or not the spectral density  $D(\omega)$  of electron-phonon coupling has a spread larger than the mean frequency of interacting phonons. Thus it appears that in these intermediate cases there are two groups of phonons, one of which is responsible for the broad band and the other for the phonon sidebands.

There seem to be three possibilities to have these two classes of phonons: (a) These phonons belong to two different branches as, for instance, optical and acoustical modes; (b) they belong to two different groups as regards spatial localization, i.e., one of them represents phonons of the normal unperturbed lattice and the other is a localized mode; (c) they belong to the same branch and have no localized character, but can be divided into two groups according to whether or not they belong to a region in the Brillouin zone around some singular point in the phonon density of states. Probably the last case is the one responsible for the peaks in the phonon sidebands in systems like MgO:V<sup>2+</sup><sup>22</sup> or LaF<sub>3</sub>:Er<sup>3+</sup>,<sup>21</sup> whereas case (b) may be responsible for the structures in KCl:Eu<sup>2+</sup>.<sup>19</sup> Wagner<sup>4</sup> discussed the case of two oscillators and gave some results of calculation. He also discussed qualitatively the case of phonon sidebands superimposed on the broad continuum and gave the first moment of each sideband.

## 5. MULTIPHONON RELAXATION PROBABILITY

From the generating function (3.13) and (3.15) Kubo and Toyozawa derived an expression<sup>14</sup> for the non-radiative transition probability in the case of strong coupling under the assumption (implicit) of large width of the spectral density of electron-phonon coupling. Although the essential feature of their result is qualitatively sufficient to explain the dependence of this probability on the energy gap between levels, we rederive it here in the other limiting case of small width of the spectral density of electron-phonon coupling in order to compare this expression with recent experi-

<sup>21</sup> See, for instance, Refs. 2 and 3.

<sup>22</sup> M. D. Sturge, Phys. Rev. **130**, 639 (1963).

<sup>23</sup> H. Kanzaki and S. Sakuragi, J. Phys. Soc. Japan **24**, 1184 (1968).

<sup>24</sup> D. B. Fitchen, H. R. Fetherman, and C. B. Pierce, Solid State Commun. **4**, 205 (1966).

<sup>19</sup> M. Wagner and W. E. Bron, Phys. Rev. **139**, A223 (1965); **139**, 233 (1965); **145**, 689 (1966).

<sup>20</sup> T. Miyakawa and S. Oyama, Phys. Letters **28A**, 206 (1968).

mental data and also with the result on the phonon sidebands discussed in the previous sections.

Thus we expand the generating function (3.15) in powers of  $g_{\pm}(t)$ :

$$f_0(t) = \exp\left(\frac{it\mathcal{E}_0}{\hbar} - g\right) \sum_{m=0}^{\infty} \frac{[g_+(t)]^m}{m!} \sum_{n=0}^{\infty} \frac{[g_-(t)]^n}{n!}, \quad (5.1)$$

$$f_{NA}^N(t) = \exp\left(\frac{it\mathcal{E}_0}{\hbar} - g\right) \frac{R^2 [g(n+1)e^{-i\omega t}]^N}{N!} \sum_{k=0}^{\infty} \frac{N!}{(N+k)!k!} [g^2 n(n+1)]^k$$

$$\times \left[ \left(1 + \frac{n(n+1)}{(2n+1)^2}\right) + n(N+k+1) \left(\frac{(n+1)}{(2n+1)} - 2g\right) / (2n+1) + \frac{gn(n+1)/(2n+1)^2}{(N+k+1)(N+k+2)} + \frac{g^{-2}(N+k)[1/(2n+1) - 2g + (N+k+1)/(2n+1)]}{(2n+1)} \right]. \quad (5.3)$$

If we use the value of the cutoff frequency for the phonons interacting with the electron of a RE ion, 350 cm<sup>-1</sup>, for instance, in LaF<sub>3</sub>, we have  $n \ll 1$  for a reasonable range of temperature ( $T \lesssim 150^\circ\text{K}$ ) and we may approximate  $f_{NA}^N(t)$  by

$$f_{NA}^N(t) = \{g^N(n+1)^N/N!\} R^2(1-N/g)^2 \times \exp[it\mathcal{E}_0/\hbar - iN\omega t], \quad (5.4)$$

and we obtain for the spectral function  $F_{NA}^N(E)$

$$F_{NA}^N(E) = \{g^N(n+1)^N/N!\} R^2(1-N/g)^2 \times \delta(E + \mathcal{E}_0 - N\hbar\omega). \quad (5.5)$$

Thus in this zero-width limit the multiphonon relaxation probability is given by

$$W_{NA}^N = (2\pi/\hbar) R^2(1-N/g)^2 \{g^N(n+1)^N/N!\} \times \delta(\mathcal{E}_0 - N\hbar\omega). \quad (5.6)$$

As we are assuming that the coupling constant  $g$  is small and also that  $n$  is not much greater than unity, the factor  $[g(n+1)]^N$  is a decreasing function of  $N$  or of  $\mathcal{E}_0 = N\hbar\omega$ . Thus we may approximate (5.6) by an exponential function of  $\mathcal{E}_0$ ;

$$W_{NA}^N = W_{NA}(\mathcal{E}_0) = (2\pi/\hbar) R^2(1-N/g)^2 e^{-\alpha \mathcal{E}_0} \delta(\mathcal{E}_0 - N\hbar\omega), \quad (5.7)$$

with

$$\alpha = (\hbar\omega)^{-1} [\ln(N/g(n+1)) - 1], \quad (5.7')$$

where we have used Stirling's formula. This expression shows that for a reasonable range of values of  $N$  we may approximate  $W_{NA}(\mathcal{E}_0)$  by an exponential function

$$W_{NA}(\mathcal{E}_0) = W_{NA}(0) e^{-\alpha \mathcal{E}_0}. \quad (5.6')$$

[The exponential dependence is only approximate because both  $\alpha$  and  $W_{NA}(0)$  depend at least implicitly on  $\mathcal{E}_0$ .]

Actually the spectral density of electron-phonon coupling  $D(\omega)$  has a finite width  $\Delta\omega$ , and we will have a

$$g_{NA}(t) = R^2 + 2R_+R_- + [(J_- - 2RR_-) + (J_+ - 2RR_+)] + R_-^2 + R_+^2. \quad (5.2)$$

If we assume for simplicity that the spectral density  $D(\omega)$  has only one singularity at some frequency  $\omega_s$ , then it is easy to show that the generating function for  $N$ -phonon processes is

line-shape function  $G_N(\omega)$  which is the  $N$ th convolution of the individual line-shape function  $G(\omega)$  instead of the  $\delta$  function in both (5.5) and (5.6). Thus we would obtain

$$W_{NA}^N = (2\pi/\hbar) R^2(1-N/g)^2 e^{-\alpha \mathcal{E}_0} G_N(0), \quad (5.8)$$

where  $G_N(0)$  is the value of  $G_N(\omega)$  at  $\omega = \mathcal{E}_0 - N\hbar\omega = 0$ .

We see that in this approximation the multiphonon relaxation probability is given by (5.6), which shows that it has an approximately exponential dependence on the energy gap between levels. Comparison with the expression for the intensity of the  $N$ th phonon sideband shows that the ratio of the spectral functions for optical absorption and for multiphonon relaxation is equal to

$$R^2(1-N/g)^2/|M|^2. \quad (5.9)$$

This ratio shows that in the case of weak coupling (small  $g$ ), the relative importance of higher multiphonon processes will be enhanced compared to that in optical absorption (or emission). Of course this does not imply that the multiphonon process is more important in the relaxation than it is in the optical spectra. The relative importance of the multiphonon process itself is determined by the ratio of matrix elements ( $|R|^2/|M|^2$ ).

## 6. PHONON-ASSISTED ENERGY-TRANSFER PROBABILITY

In this section we extend the formalism used in previous sections to calculate the probability of phonon-assisted energy transfer between two ions  $a$  and  $b$ . Although most of the notation defined in Sec. 2 still applies to this case, one must recall that neither the initial nor the final state of our system is the ground state. We denote the initial and final states by

$$j = (j_a^*, j_b) \quad \text{and} \quad k = (k_a, k_b^*),$$

respectively, where  $j_a^*$  and  $k_b^*$  denote the excited states

of ions  $a$  and  $b$  and  $k_a$  and  $j_b$  denote the corresponding ground states of these ions.

Next we note that the electron-lattice interaction Hamiltonian has the form

$$H_{eL}(r, Q) = -\sum_s [V_s(r_1) + V_s(r_2)] Q_s. \quad (6.1)$$

This interaction leads directly to the result in which the displacement of the equilibrium position of the normal modes, i.e., the corresponding parameter  $\Delta_s$  defined by (3.19) is given by

$$\Delta_s = [(V_{sj_a^*j_a^*} - V_{sk_a k_a}) - (V_{sj_b^*j_b^*} - V_{sj_b j_b})] / \omega_s^2, \quad (6.2)$$

that is, it is a difference between two terms representing the interaction of ions  $a$  and  $b$  with the lattice vibrations, and each of these terms is the difference between the matrix element in the ground and excited state of these ions. Thus unless  $V_{sj_a^*j_a^*} - V_{sk_a k_a}$  and  $V_{sj_b^*j_b^*} - V_{sj_b j_b}$  differ in their sign (which seems to be quite improbable insofar as ions  $a$  and  $b$  are ions of similar kind), lattice modes which interact equally with both ions do not give a large contribution to  $\Delta_s$ .

One may construct interaction modes<sup>5</sup>  $q_{ai}$  and  $q_{bi}$  instead of the normal modes  $Q_s$  in such a way that modes  $q_{ai}$  interact strongly with only ion  $a$ , whereas modes  $q_{bi}$  interact strongly only with ion  $b$ . These interaction modes do not diagonalize the lattice potential, but the off-diagonal terms can be incorporated into the anharmonic effect. In one extreme case, in which each electron is localized on an ion interacting strongly with lattice vibrations to form localized modes of large amplitude near that ion, it is quite natural to expect that each electron interacts with different modes of vibration, although the frequencies of these modes may be close to each other.

Therefore we understand in this section that the transformation to these interaction modes has already been made. Then one can divide the spectral density of electron-phonon coupling  $D(\omega)$  into two parts,

$$D(\omega) = D_a(\omega) + D_b(\omega), \quad (6.3)$$

and it is easy to show that the generating function  $f_{ab}(t)$  can be decomposed into three parts:

$$f_{ab}(t) = |H_{ab}|^2 \exp(it\mathcal{E}_0/\hbar) f_{0a}(t) f_{0b}(t), \quad (6.4)$$

$$f_{0a}(t) = \exp[-g_a + g_{a+}(t) + g_{a-}(t)], \quad (6.5)$$

$$g_{a\pm}(t) = \int d\omega D_a(\omega) \left\{ \begin{matrix} n_\omega \\ n_\omega + 1 \end{matrix} \right\} e^{\pm i\omega t}, \quad (6.6)$$

$$g_a = g_{a+}(0) + g_{a-}(0),$$

with corresponding expressions for  $g_b$ ,  $g_{b\pm}(t)$ , and  $f_{0b}(t)$ .

Thus in this case it is also legitimate to write the expression for the probability of energy transfer in the form

$$W_{ab} = (2\pi/\hbar) |H_{ab}|^2 S_{ab}, \quad (6.7)$$

where  $S_{ab}$  is the overlap of line-shape functions for absorption of ion  $b$  and emission of ion  $a$ . Thus the original form of the energy transfer probability<sup>12</sup> is retained. It is important to note that in this case we must include the phonon sidebands in the line shape to be used in the evaluation of  $S_{ab}$ .

Now in the weak-coupling limit, which is of greatest interest to us for RE ions, we expand the line-shape function into multiphonon components. If the energy transfer under consideration requires emission of  $N$  phonons for energy conservation, and if we assume that the frequencies of the average phonon involved in the process are equal to each other, the  $N$ -phonon part of the overlap  $S_{ab}^N$  ( $S_{ab} = \sum_N S_{ab}^N$ ) can be written in the following form:

$$S_{ab}^N = \sum_{k=0}^N \sigma_{ab}(N-k, k; 0), \quad (6.8)$$

where

$$\sigma_{ab}(m, n; E) = \int f_a^m(E-E') f_b^n(E') dE' \quad (6.9)$$

is the overlap between the  $m$ -phonon emission line shape of ion  $a$  and the  $n$ -phonon absorption line shape of ion  $b$ .

In the limit of vanishing width of the density function  $D(\omega)$ , the generating function for the  $N$ -phonon process is, assuming equal mean frequency of interacting phonon modes for both ions  $a$  and  $b$ ,

$$f_0^N(t) = f_{0a}^N(t) e^{-\theta b} (1 + g_b/g_a)^N. \quad (6.10)$$

Inserting (6.10) and (6.7) we have

$$W_{ab} = (2\pi/\hbar) |H_{ab}|^2 \sum_{N=0}^{\infty} F_a^N(0) e^{-\theta b} (1 + g_b/g_a)^N, \quad (6.11)$$

$$F_a^N(E) = [g_a^N (n+1)^N / N!] \delta(E + \mathcal{E}_0 - N\hbar\omega). \quad (6.12)$$

So in this limit of weak coupling the ratio of the  $N$ th multiphonon transition probability for energy transfer to that of the relaxation process is

$$(|H_{ab}|^2 / |R|^2) e^{-\theta b} (1 + g_b/g_a)^N (1 - N/g_a)^{-2}. \quad (6.13)$$

As we are assuming that  $g_a$  and  $g_b$  are small, the re-normalization factor  $e^{-\theta b}$  will not be important. Also the factor  $(1 - N/g_a)^2$  varies much more slowly than exponentially with  $N$ . Thus in the case of energy transfer the relative importance of the  $N$ -phonon process is enhanced by a factor  $(1 + g_b/g_a)^N$  compared with that for the relaxation process.

Returning to the actual case of nonzero linewidth, we can simplify the formulas (6.8) and (6.9) when we assume that linewidths are small compared with the mean phonon frequency  $\bar{\omega}$  and ignore the rather slow dependence of the width on the order of convolution mentioned in Sec. 4. Thus the overlap integrals can be



approximated by

$$\sigma_{ab}(m, n; E) \cong (g_a^m g_b^n / m! n!) e^{-(g_a + g_b)} \sigma_{ab}(0, 0; E). \quad (6.14)$$

and  $W_{ab}$  can be put in the following form:

$$W_{ab} = (2\pi/\hbar) |H_{ab}|^2 \sum_N e^{-(g_a + g_b)} [(g_a + g_b)^N / N!] \times \sigma_{ab}(0, 0; E) \delta(N, \mathcal{E}_0/\hbar\omega). \quad (6.15)$$

When we compare this expression with the corresponding expression (5.6') or (5.7) one can easily show that  $W_{ab}$  can be written in the form

$$W_{ab}(\mathcal{E}_0) = W_{ab}(0) e^{-\beta \mathcal{E}_0}, \quad (6.16)$$

with

$$W_{ab}(0) = (2\pi/\hbar) |H_{ab}|^2 \sigma_{ab}(0, 0; E) e^{-(g_a + g_b)}, \quad (6.17)$$

$$\beta = \alpha - \gamma, \quad (6.18)$$

$$\gamma = (\hbar\omega)^{-1} \ln(1 + g_b/g_a). \quad (6.19)$$

If we assume that  $g_a = g_b$  and use experimental values of  $\hbar\omega \sim 350 \text{ cm}^{-1}$  and  $\alpha \sim 5 \times 10^{-3} \text{ cm}$  for  $\text{RE}^{3+}$  ions in  $\text{LaF}_3$ ,<sup>7</sup> then we have

$$\gamma \sim 2 \times 10^{-3} \text{ cm}$$

and  $\beta$  will be reduced by almost a factor of 2 compared to  $\alpha$ . Thus the dependence of the transfer probability on the difference  $\delta E$  in the excitation energies of ions  $a$  and  $b$  will be formally the same as the dependence of the multiphonon relaxation probability on the energy gap  $\Delta E$  between adjacent electronic levels.

Since absorption and emission spectra are seldom measured to the precision necessary for the evaluation of the density of states factor  $S_{ab}$  in the energy-transfer process, this correspondence can be extremely useful in estimating  $S_{ab}$  from multiphonon relaxation probabilities.

## 7. SUMMARY AND DISCUSSIONS

The results of the preceding sections show that probabilities for multiphonon relaxation of excited states as well as for phonon-assisted energy transfer between ions can be written in terms of the  $N$ -fold convolution of the phonon sideband line shape which is observed in emission or absorption, where  $N$  is the smallest number of phonons which make up the energy mismatch. In the case of energy transfer there can be various ways of allocating  $N$  phonons to either of the two ions, and this accounts for an extra factor  $(1 + g_b/g_a)^N$  in (6.11).

The result that the transfer probability can be written in terms of an overlap of absorption and emission line shapes of activator and sensitizer ions, respectively, was to have been expected from the general

result derived from conservation of energy considerations many years ago.<sup>12</sup> What is new in our present result is that as it takes advantage of the multiphonon sidebands explicitly, the transfer probability can be shown to depend exponentially on the energy gap in just the same way as the multiphonon relaxation probability. This dependence is confirmed experimentally for the multiphonon relaxation processes and may be used to estimate the transfer probability between ions with different excitation energies.<sup>11</sup>

A theoretical estimate of the critical value  $\Delta E_c$  of the energy gap below which the fluorescence between the corresponding levels cannot be observed is difficult at the present stage of our knowledge about various parameters characterizing the interactions. However, if we use empirical values for relaxation rates extrapolated to zero gap  $W_{NA}(0)$ , a typical value of emission probability  $W_{em}$  and the coefficient of exponent  $\alpha$  in the equation

$$W_{NA}(\mathcal{E}_0) = W_{NA}(0) \exp(-\alpha \mathcal{E}_0), \quad (7.1)$$

one can make a rough estimate of  $\Delta E_c$  from

$$\Delta E_c = \alpha^{-1} \ln[W_{NA}(0)/W_{em}]. \quad (7.2)$$

In the case of  $\text{LaF}_3:\text{Er}^{3+}$ , in which most detailed information is available,  $\alpha = 5 \times 10^{-3} \text{ cm}$  and the extrapolated value to zero gap is  $W_{NA}(0) = 1 \times 10^8 \text{ sec}^{-1}$ .<sup>7</sup> If we assume as a typical radiative decay rate  $W_{em} \sim 10^3 \text{ sec}^{-1}$ ,<sup>6</sup> we get  $\Delta E_c$  of the order of  $2300 \text{ cm}^{-1}$ . This estimate seems to be in reasonable agreement with the value quoted, i.e.,  $\sim 1600 \text{ cm}^{-1}$ .<sup>6</sup>

The basic assumption in our treatment of the problem is that the adiabatic approximation is valid and that the most important contribution to the probabilities comes from the diagonal (in electronic states) part of the electron-phonon interaction  $H_{eL}$ , which is assumed to be linear in the lattice coordinates.

The adiabatic approximation will be good as long as the energy difference between successive levels is larger than the phonon energy involved, so that the correction in first order of the electronic wave function is small. The off-diagonal (in electronic states) matrix elements which contribute to the nonadiabatic part of the Hamiltonian also contribute to the second-order energy correction quadratic in lattice coordinates. Such quadratic terms which may also derive from the quadratic part of the electron-lattice interaction are responsible for the shift of frequencies of multiphonon components in emission and absorption. Although there is some evidence that anharmonic terms affect the temperature dependence of the zero-phonon line characteristics in  $\text{RE}^{2+}$  ions in alkali halides<sup>25</sup> there seem to be no observable effects of this kind in trivalent RE ions.

<sup>25</sup> G. Baldini and M. Guzzi (unpublished).