DESCRIPTION OF NONRADIATIVE MULTIPHONON TRANSITIONS IN THE STATIC COUPLING SCHEME

II. APPROXIMATIONS

R. PÄSSLER

Technische Hochschule, Sektion Physik-Elektronische Bauelemente, Karl-Marx-Stadt)*

For sufficiently large phonon dispersion the general rate-expression for nonradiative multiphonon transitions reduces to a gentle analytical approximate expression suitable, due to its compactness, for numerical calculations too. Simple explicit formulae are obtained in classical and semiclassical approximation frequently used in earlier papers, the severe limitations imposed to their actual applicability being discussed. On the basis of the concept of a mean phonon energy effective at medium temperatures, we derive explicit overlap-factor formulae applying to the experimentally most typical cases when the spacings of the electronic levels involved in the nonradiative multiphonon transitions considered are larger than the corresponding readjustment energies of the phonon field by a factor $10^{1/2}$.

1. INTRODUCTION

For a dynamical electronic system coupled statically with a dissipative system of quantized harmonic oscillators being in a state of thermal equilibrium, a general rate expression for nonradiative multiphonon transitions induced by the nonstatic part of the electron-phonon interaction had been given in a first paper [1]. According to the pattern of the simple transition-rate formula obtained there for the singular case of completely vanishing phonon dispersion, we shall derive in the present paper equally practicable transition-rate formulae for sufficiently large phonon dispersion.

Thus, having established in sec. 2 a connection between the most important ones of the quantities determining the spectral behaviour of the temperature-averaged overlap factor with the corresponding experimental luminescence spectra data, we give in sec. 3 some fundamental analytical properties of the overlap factor being a smooth function of the magnitude of heat conversion. These preliminary investigations allow us to write down in sec. 4 an approximate rate expression which, due to its compactness, gentleness and large range of applicability, suffices within the framework of the static coupling scheme for the great majority of applications.

In sec. 5 we specialize this nearly exact rate expression for both the classical and the semiclassical approximation frequently used in earlier work based on the adiabatic coupling scheme, see e.g. LAX [2], RICKAYZEN [3], STASIW [4], PERLIN [5], SINYAVSKIY and KOVARSKIY [6], BONCH-BRUEVICH [7]. Having discussed the severe limitations of such elementary approximations which forbid, practically, their use for a very large class of nonradiative multiphonon transitions being of major physical interest, we pass in sec. 6 to higher approximations based essentially on the concept

*) *Strasse der Nationen 62, 90 Karl-Marx-Stadt, DDR.*

of a mean phonon energy effective at medium temperatures. This procedure enables us to give, in the first line, a theoretically underpined derivation of the single-phonon-energy formula (I. 6. 4) attained, in a merely intuitive way, in [1]. Yet, beyond this, there will be obtained a modified effective-phonon-energy formula for the smooth overlap factor which, in addition to accounting generally for the characteristic slow descent of its functional behaviour on the extremely far high-energy wing, reproduces correctly the three nontrivial lowest-order moments (i.e. the center of gravity, the broadening and the skewness) of the exact overlap-factor curve.

2. OVERLAP-FACTOR MOMENTS

The temperature-averaged rates $w_{Na'a}$ and $w_{Ra'a}$ of nonradiative and radiative multiphonon transitions $|a\rangle \to |a'\rangle$ of a dynamical electronic system coupled statically (within a linear interaction law) to a dissipative system N of quantized harmonic oscillators had been expressed in [1] in terms of the temperature-averaged overlap factors

$$\mathscr{R}_{a'a}(E) = \frac{1}{2\pi \mathrm{i}} \int_{-\mathrm{i}\infty}^{+\mathrm{i}\infty} r_{a'a}(\lambda)\, \mathrm{e}^{-\lambda E}\, \mathrm{d}\lambda \tag{2.1}$$

with quasicontinuously varying argument E corresponding to the energy converted into heat by means of an attached multiphonon relaxation process. The associated generating function

$$r_{a'a}(\lambda) = \int_{-\infty}^{+\infty} \mathscr{R}_{a'a}(E)\, \mathrm{e}^{\lambda E}\, \mathrm{d}E \tag{2.2}$$

corresponding to the Laplace transform of $\mathscr{R}_{a'a}(E)$ reads explicitly

$$r_{a'a}(\lambda) = \exp\left(s_{Na'a}(\lambda) - s_{Na'a}(0)\right), \tag{2.3}$$

$$s_{Na'a}(\lambda) \equiv \sum_n \varepsilon_n^{-1} S_{na'a} \cdot \left(\sinh \frac{\varepsilon_n}{2kT}\right)^{-1} \cdot \cosh\left(\frac{\varepsilon_n}{2kT} + \lambda\varepsilon_n\right) = \tag{2.4}$$

$$= s_{Na'a}(0) + \sum_{m=1}^{\infty} \frac{1}{m!} \cdot S_{a'a}^{(m)} \lambda^m,$$

where $\varepsilon_n > 0$ and $S_{na'a} \geqq 0$ are the phonon energy and the transition-specific readjustment energy, resp., of the n-th normal mode, T is the temperature of the phonon field, k is the Boltzmann constant, and by

$$S_{a'a}^{(2p+1)} \equiv \sum_n \varepsilon_n^{2p} S_{na'a} \tag{2.5a}$$

and

$$S_{a'a}^{(2p+2)} \equiv \sum_n \varepsilon_n^{2p+1} S_{na'a} \coth \frac{\varepsilon_n}{2kT}, \tag{2.5b}$$

$p = 0, 1, 2, \ldots$, we have denoted the temperature-independent odd-order and the temperature-dependent even-order derivatives, resp., of the function $s_{Na'a}(\lambda)$ at $\lambda = 0$ which correspond to the semi-invariants of the spectral distribution of the overlap-factor curve (2.1), cf. KUBO and TOYOZAWA [8], MCCUMBER [9]. Expanding the latter derivatives in terms of the former ones, we obtain the series

$$S_{a'a}^{(2p+2)} = 2kT \cdot \sum_{l=0}^{\infty} \frac{f^{(2l)}}{(2l)!} \cdot \left(\frac{1}{2kT}\right)^{2l} S_{a'a}^{(2p+2l+1)} \tag{2.6}$$

quickly converging at high and medium temperatures, where we have denoted by $f^{(2l)}$, $l = 0, 1, \ldots$, the even-order derivatives of the function $f(x) \equiv x \cdot \coth x$ at $x = 0$.

Differentiating now expression (2.2) m-times with respect to λ and putting then $\lambda = 0$, we obtain for the moments $r_{a'a}^{(m)}$ of the overlap-factor curve $\mathscr{R}_{a'a}(E)$ (moments of heat conversion) exactly

$$r_{a'a}^{(m)} \equiv \int_{-\infty}^{+\infty} E^m \mathscr{R}_{a'a}(E)\, \mathrm{d}E = \frac{\mathrm{d}^m}{\mathrm{d}\lambda^m} \exp\left(s_{Na'a}(\lambda) - s_{Na'a}(0)\right)\Big|_{\lambda=0} \tag{2.7}$$

At this, the zeroth-order moment $r_{a'a}^{(0)} = 1$ reproduces the usual normalization condition of the overlap factor $\mathscr{R}_{a'a}(E)$ (cf. [1]), and the first-order moment (center of gravity) $r_{a'a}^{(1)} = S_{a'a}^{(1)}$ corresponding to the half value of the Stokes' shift (see e.g. PEKAR [10], PERLIN [5]) is just identical with the transition-specific readjustment energy $\sum_n S_{na'a}$ of the phonon field (cf. [1]). The latter quantity may be considered to be generally the most important one of the parameters determining the rate of nonradiative multiphonon transitions (cf. KUBO [11]). In the case of nonvanishing phonon dispersion considered here it is to take over the role of the well-known dimensionless Huang-Rhys parameter $\sum_n \varepsilon_n^{-1} S_{na'a}$ (see e.g. HUANG and RHYS [12], MEYER [13], DEXTER [14], HOWGATE [15]), a quantity becoming less important with increasing phonon dispersion.

In passing for $m = 2, 3, 4, \ldots$ from (2.7) to moments $\varrho_{a'a}^{(m)}$ referring to the center of gravity $S_{a'a}^{(1)}$ of $\mathscr{R}_{a'a}(E)$, we obtain from (2.2) correspondingly

$$\varrho_{a'a}^{(m)} \equiv \int_{-\infty}^{+\infty} (E - S_{a'a}^{(1)})^m \mathscr{R}_{a'a}(E)\, \mathrm{d}E = \frac{\mathrm{d}^m}{\mathrm{d}\lambda^m} \exp\left(s_{Na'a}(\lambda) - s_{Na'a}(0) - \lambda S_{a'a}^{(1)}\right)\Big|_{\lambda=0} \tag{2.8}$$

so that we have, in particular, $\varrho_{a'a}^{(2)} = S_{a'a}^{(2)}$ for the broadening, $\varrho_{a'a}^{(3)} = S_{a'a}^{(3)}$ for the skewness and $\varrho_{a'a}^{(4)} = S_{a'a}^{(4)} + 3(S_{a'a}^{(2)})^2$ for the kurtosis of the overlap-factor curve $\mathscr{R}_{a'a}(E)$ (cf. LAX [2], STASIW [4]).

For an experimental determination of the low-order quantities $S_{a'a}^{(m)}$ (2.5) in (2.7) or (2.8), $m = 1, 2, 3, \ldots$, we consider the normalized spectral behaviour of the associated luminescence band (see e.g. LAX [2], PERLIN [5]), which, in being located

at photon energies $\varepsilon \gg kT$, is approximately given by the function $\mathscr{R}_{a'a}(|\mathscr{J}_{a'} - \mathscr{J}_a| - \varepsilon)$ (2.1) with the spacing $|\mathscr{J}_{a'} - \mathscr{J}_a|$ of the effective energy levels (see [1]) of the electronic system in its base states $|a'\rangle$ and $|a\rangle$. Thus, the moments $L^{(m)}_{a'a}$ and $\Lambda^{(m)}_{a'a}$ of the luminescence band which refer to the origin $\varepsilon = 0$ and the center of gravity $\varepsilon = L^{(1)}_{a'a}$, resp., are connected with the corresponding moments $r^{(m)}_{a'a}$ and $\varrho^{(m)}_{a'a}$ of heat conversion approximately by

$$L^{(m)}_{a'a} \doteq \sum_{m'=0}^{m} \frac{m!}{m'!\,(m-m')!} (-1)^{m'} r^{(m')}_{a'a} |\mathscr{J}_{a'} - \mathscr{J}_a|^{m-m'} \tag{2.9}$$

and

$$\Lambda^{(m)} \doteq (-1)^m \varrho^{(m)}_{a'a} \tag{2.10}$$

so that we have according to (2.6) for the two nontrivial lowest-order moments in particular

$$L^{(1)}_{a'a} \doteq |\mathscr{J}_{a'} - \mathscr{J}_a| - S^{(1)}_{a'a} \tag{2.11}$$

$$\Lambda^{(2)}_{a'a} \doteq S^{(2)}_{a'a} = 2kT\left[S^{(1)}_{a'a} + \frac{1}{3}\left(\frac{1}{2kT}\right)^2 S^{(3)}_{a'a} + \ldots\right]. \tag{2.12}$$

Consequently, on the basis of the temperature-behaviour of the broadening $\Lambda^{(2)}_{a'a}$ of the luminescence band at high and medium temperatures we can successively determine the quantities $S^{(1)}_{a'a}$ and $S^{(3)}_{a'a}$, the combination

$$\varepsilon_{a'a} \equiv \left(\frac{S^{(3)}_{a'a}}{S^{(1)}_{a'a}}\right)^{1/2} \tag{2.13}$$

of both giving some transition-specific phonon energy effective at temperatures T of the order of the corresponding Debye temperature $T_{a'a} \equiv \varepsilon_{a'a}/k$ which will play an essential part in the approximation procedures presented in sec. 6. Eventually, the energy spacing $|\mathscr{J}_{a'} - \mathscr{J}_a|$ of the effective electronic levels may be determined from the location of the center of gravity $L^{(1)}_{a'a}$ of the luminescence band.

3. SMOOTH OVERLAP FACTORS

In typical nonradiative multiphonon band-imperfection transitions of carriers in semiconductors the heat energy $|E| \doteq |\mathscr{J}_{a'} - \mathscr{J}_a|$, interchanged with the dissipative system of lattice modes n, is generally larger than the corresponding phonon energies ε_n by a factor of the order $10^1 \ldots 10^2$ so that the condition (I. 6. 1) of the smoothness of the overlap-factor curve is usually fulfilled even in the case of relatively small phonon dispersion (e.g. for the field of only the longitudinal optical modes in heteropolar crystals, see KRIVOGLAZ and PEKAR [16]). Consequently, in an approximate calculation of the integral (2.1) within the well-known saddle-point approximation

(see e.g. [16]) just the immediate vicinity of the real saddle point $\lambda_{a'a}(E)$ of the exponential function $\exp\left(s_{Na'a}(\lambda) - s_{Na'a}(0) - \lambda E\right)$ in (2.1),

$$s^{(1)}_{Na'a}(\lambda_{a'a}(E)) = E \tag{3.1}$$

gives the dominating contribution to the integral (2.1) so that the overlap factor reduces to the smooth function

$$\mathscr{R}_{a'a}(E) \doteq \left[2\pi s^{(2)}_{Na'a}(\lambda_{a'a}(E))\right]^{-1/2} \exp\left[\Phi_{a'a}(E)\right] \equiv \bar{\mathscr{R}}_{a'a}(E) \tag{3.2}$$

of the heat energy E (cf. [16, 5]), where

$$\Phi_{a'a}(E) \equiv s_{Na'a}(\lambda_{a'a}(E)) - s_{Na'a}(0) - \lambda_{a'a}(E)\, E\,. \tag{3.3}$$

To derive first of all a general relationship connecting smooth overlap factors $\bar{\mathscr{R}}_{a'a}(E)$ with arguments $E = \pm|E|$ differing only in their sign, we start from a corresponding symmetry relation

$$\lambda_{a'a}(E) = \frac{E}{|E|}\left(\lambda_{a'a}(|E|) + \frac{1}{2kT}\right) - \frac{1}{2kT} = -\lambda_{a'a}(-E) - \frac{1}{kT} \tag{3.4}$$

obviously satisfied by the real solution of eq. (3.1), from which it follows immediately that the quantity $s^{(2)}_{Na'a}(\lambda_{a'a}(E))$ in the preexponential factor in (3.2) remains unchanged when the sign of E is converted and the function $\Phi_{a'a}(E)$ in the exponential of (3.2) obeys a symmetry relation

$$\Phi_{a'a}(E) = \Phi_{a'a}(|E|) + \frac{E - |E|}{2kT} = \Phi_{a'a}(-E) + \frac{E}{kT}\,. \tag{3.5}$$

Thus, for the smooth overlap factor $\bar{\mathscr{R}}_{a'a}(E)$ (3.2) itself we have a relationship

$$\bar{\mathscr{R}}_{a'a}(E) = \bar{\mathscr{R}}_{a'a}(|E|) \exp\left(\frac{E - |E|}{2kT}\right) = \bar{\mathscr{R}}_{a'a}(-E) \exp\left(\frac{E}{kT}\right) \tag{3.6}$$

generally holding for the exact overlap factor $\bar{\mathscr{R}}_{a'a}(E)$ (2.1) too (cf. [1]), which allows us principially to confine ourselves in explicit calculations of $\bar{\mathscr{R}}_{a'a}(E)$ to positive arguments.

In order to express now the overlap factor $\bar{\mathscr{R}}_{a'a}(E)$ (3.2) with given energy E in terms of the solution of eq. (3.1) for an energy E_0 differring from E in magnitude, we differentiate (by observing (3.1)) the function $\Phi_{a'a}(E)$ (3.3) m-times with respect to E, obtaining

$$\Phi^{(m)}_{a'a}(E) = -\lambda^{(m-1)}_{a'a}(E)\,, \tag{3.7}$$

$m = 1, 2, 3, \ldots$, where the low-order derivatives of $\lambda_{a'a}(E)$ read explicitly

$$\lambda^{(1)}_{a'a}(E) = \frac{1}{s^{(2)}_{Na'a}(\lambda_{a'a}(E))}\,, \quad \lambda^{(2)}_{a'a}(E) = \frac{-\,s^{(3)}_{Na'a}(\lambda_{a'a}(E))}{\left[s^{(2)}_{Na'a}(\lambda_{a'a}(E))\right]^3}\,, \ldots \tag{3.8}$$

(see [16]). Expanding now the functions $\Phi_{a'a}(E)$ (3.3) and $[s^{(2)}_{Na'a}(\lambda_{a'a}(E))]^{-1} = \lambda^{(1)}_{a'a}(E)$ (3.8) in (3.2) into Taylor series we can immediately write

$$\bar{\mathcal{R}}_{a'a}(E) = \left\{1 + [\lambda^{(1)}_{a'a}(E_0)]^{-1} \sum_{m=1}^{\infty} \frac{1}{m!} \lambda^{(m+1)}_{a'a}(E_0)\,(E - E_0)^m\right\}^{1/2} \cdot \exp\left\{-\sum_{m=1}^{\infty} \frac{1}{m!} \lambda^{(m-1)}_{a'a}(E_0)\,(E - E_0)^m\right\} \bar{\mathcal{R}}_{a'a}(E_0)\,, \tag{3.9}$$

this expansion permitting us, in particular, to reduce overlap factors $\bar{\mathcal{R}}_{a'a}(E)$ with slightly varying heat energies $E \approx E_0$ in a very elegant manner (see sec. 4) to a product of an overlap factor $\bar{\mathcal{R}}_{a'a}(E_0)$ at fixed heat energy E_0 with some less crucial factor of the order of magnitude 10^0.

Now, if for given difference $E - E_0$ of heat energies the condition

$$\varepsilon_n \frac{|E - E_0|}{s^{(2)}_{Na'a}(\lambda_{a'a}(E_0))} \ll 1 \tag{3.10}$$

is fulfilled with the phonon energies ε_n of the individual normal modes n, the contributions of the $\lambda^{(m)}_{a'a}(E_0)$-terms, $m = 2, 3, \ldots$, to (3.9) are negligibly small in comparison with the $\lambda^{(1)}_{a'a}(E_0)$-term in the exponential, and in this approximation we have simply

$$\bar{\mathcal{R}}_{a'a}(E) \doteq \exp\left\{-\lambda_{a'a}(E_0)\,(E - E_0) - \frac{(E - E_0)^2}{2s^{(2)}_{Na'a}(\lambda_{a'a}(E_0))}\right\} \bar{\mathcal{R}}_{a'a}(E_0)\,. \tag{3.11}$$

Solving eq. (3.1) explicitly what can be done exactly for heat energies $|E_0| = S^{(1)}_{a'a}$ and 0,

$$\lambda_{a'a}(S^{(1)}_{a'a}) = 0 \quad \text{and} \quad \lambda_{a'a}(0) = -\frac{1}{2kT}\,, \tag{3.12}$$

we may, by confining ourselves to formula (3.11) (in simplest approximation) or by starting directly from formula (3.9) (in higher approximation), immediately write down less or more gentle explicit overlap-factor formulae for heat energies $|E| \approx S^{(1)}_{a'a}$ being of interest in radiative multiphonon transitions as well as energies within a physically less interesting energy range $|E| \approx 0$. Contrary to this, for energies $|E|$ large in comparison with the readjustment energy of the phonon field which are usually of interest in nonradiative multiphonon transitions, such a formal reduction of $\bar{\mathcal{R}}_{a'a}(|E|)$ to $\bar{\mathcal{R}}_{a'a}(S^{(1)}_{a'a})$ or even to $\bar{\mathcal{R}}_{a'a}(0)$ would be without use in general due to the relatively slow convergence (see also KRIVOGLAZ [17]) of the series in (3.9) in the latter case.

4. NONRADIATIVE MULTIPHONON TRANSITION RATES

If the variations $\delta E \equiv E - E_0$ of the energy E in (3.11) around a fixed value E_0 is as small as the order of magnitude of the phonon energies, $|\delta E| \approx \varepsilon_n$, so that the condition (3.10) reduces to the inequality

$$\varepsilon_n^2 \ll s^{(2)}_{Na'a}(\lambda_{a'a}(E_0)) \tag{4.1}$$

nearly coinciding with the criterion of the applicability of the saddle-point approximation (see e.g. [16, 5]), the quadratic term in the exponential in (3.11) gives only a small negative correction to unity,

$$\bar{\mathcal{R}}_{a'a}(E_0 + \delta E) \doteq \left[1 - \frac{(\delta E)^2}{2 s^{(2)}_{Na'a}(\lambda_{a'a}(E_0))}\right] \exp\left[-\lambda_{a'a}(E_0)\,\delta E\right] \bar{\mathcal{R}}_{a'a}(E_0)\,. \tag{4.2}$$

In this approximation (cf. a corresponding rougher one used by KRIVOGLAZ [17] where the small quadratic term had been omitted completely) we obtain for the probability $w_{Na'a}$ (I.4.21) of a nonradiative multiphonon transition $|a\rangle \to |a'\rangle$ of the electronic system per unit time generally the compact expression

$$w_{Na'a} \doteq \frac{2\pi}{\hbar} \left\{ \left| a_{Na'a} - b^{(0)}_{Na'a}(\lambda_{a'a}(\mathscr{J}_a - \mathscr{J}_{a'})) \right|^2 + \right. \tag{4.3}$$

$$\left. + c^{(0)}_{Na'a}(\lambda_{a'a}(\mathscr{J}_a - \mathscr{J}_{a'})) - \frac{\left| b^{(1)}_{Na'a}(\lambda_{a'a}(\mathscr{J}_a - \mathscr{J}_{a'})) \right|^2}{s^{(2)}_{Na'a}(\lambda_{a'a}(\mathscr{J}_a - \mathscr{J}_{a'}))} \right\} \bar{\mathcal{R}}_{a'a}(\mathscr{J}_a - \mathscr{J}_{a'})$$

with the real solution $\lambda_{a'a}(E_0)$ of eq. (3.1) and the smooth overlap factor $\bar{\mathcal{R}}_{a'a}(E_0)$ (3.2) for an energy E_0 equal to the difference $\mathscr{J}_a - \mathscr{J}_{a'}$ of the effective energy levels of the electronic system in the initial and final state. At this, the λ-derivatives of the functions $b_{Na'a}(\lambda)$, $c_{Na'a}(\lambda)$ and $s_{Na'a}(\lambda)$ in (4.3) are explicitly given by

$$\left.\begin{matrix} b^{(m)}_{Na'a}(\lambda) \\ c^{(m-1)}_{Na'a}(\lambda) \\ s^{(m+1)}_{Na'a}(\lambda) \end{matrix}\right\} = \sum_n \varepsilon_n^m \left\{\begin{matrix} B_{na'a} \\ C_{na'a} \\ S_{na'a} \end{matrix}\right\} \frac{\exp\left[+\varepsilon_n\left(\frac{1}{2kT} + \lambda\right)\right] - (-1)^m \exp\left[-\varepsilon_n\left(\frac{1}{2kT} + \lambda\right)\right]}{2 \sinh \frac{\varepsilon_n}{2kT}}, \tag{4.4}$$

$m = 0, 1, \ldots$, with the transition-specific energy coefficients $B_{na'a}$, $C_{na'a} \geqq 0$ and $S_{na'a} \geqq 0$ which are, according to their definition (I.4.8), generally connected by the relation

$$|B_{na'a}|^2 = C_{na'a}\, S_{na'a}\,. \tag{4.5}$$

Thus, we have now at our disposal for the relevant case (I.6.1) of sufficiently large phonon dispersion a transition-rate formula (4.3) which, like expression (I.5.19)

derived for vanishing phonon dispersion, reduces to a product of a single overlap factor (3.2) with some transition-specific terms being weakly dependent (according to low-order power laws, cf. [1]) on the given value $E_0 = \mathscr{J}_a - \mathscr{J}_{a'}$ of the energy converted into heat. It is because of the simplicity, the gentleness and the large range of applicability of formula (4.3) that it can be made to serve, within the framework of the static coupling scheme, as a starting point for the majority of typical nonradiative multiphonon transition-rate calculations.

In this connection we wish to point out that such a gentle approximation formula could not have been obtained in evaluating $w_{Na'a}$ directly from (I.4.3) by putting simply $\lambda \to \lambda_{a'a}(\mathscr{J}_a - \mathscr{J}_{a'})$ in the preexponential factor in (I.4.6), as one would be possibly inclined to do in a roughest approximation. Such a procedure would not give the characteristic negative term (cf. e.g. [17]) the occurence of which only completes the formal correspondence of (4.3) with (I.5.19).

At the same time, as to be required with respect to any approximate transition-rate expression, the appearance of such a negative term does not affect the positive definiteness of the total expression (4.3) due to a corresponding Schwarz' type inequality

$$|b^{(1)}_{Na'a}(\lambda)|^2 \leqq c^{(0)}_{Na'a}(\lambda)\, s^{(2)}_{Na'a}(\lambda) \tag{4.6}$$

following, for any real λ, immediately from relation (4.5) in connection with the definition (4.4) of the functions considered.

Again, on the basis of the symmetry relations $a_{Naa'} = a^*_{Na'a}$, $B_{naa'} = -B^*_{na'a}$, $C_{naa'} = C_{na'a}$ and $S_{naa'} = S_{na'a}$ following from the actual definition (I.4.8) of these transition-specific energy coefficients in connection with the symmetry relations (3.4) and (3.6) satisfied by the position $\lambda_{a'a}(E)$ of the real saddle point and the associated smooth overlap factor $\bar{\mathscr{R}}_{a'a}(E)$, resp., it can be easily realized that the general transition-rate expression given here (as well as the more specialized ones to be deduced in sec. 5) obeys exactly the relation (I.4.11) of detailed balance,

$$\frac{w_{Naa'}}{w_{Na'a}} = \exp\left(\frac{\mathscr{J}_{a'} - \mathscr{J}_a}{kT}\right). \tag{4.7}$$

5. INFERIOR APROXIMATIONS

For energies $|E| = |\mathscr{J}_{a'} - \mathscr{J}_a|$ being of the order of magnitude of the readjustment energy $S^{(1)}_{a'a}$ of the phonon field, simple explicit transition-rate formulae can be given. The corresponding smooth overlap-factor curves reduce to normalized Gaussians

$$G(\Delta; \overline{\Delta^2}) \equiv [\pi\, 2\overline{\Delta^2}]^{-1/2} \exp\left[-\frac{\Delta^2}{2\overline{\Delta^2}}\right], \tag{5.1}$$

where Δ are the distances considered from the given center of gravity and $\overline{\Delta^2}$ are the associated mean square deviations.

5.1. Classical approximation

If at high temperatures, $\varepsilon_n \ll 2kT$, the inequality

$$\varepsilon_n \frac{|E|}{2kTS^{(1)}_{a'a}} \ll 1 \tag{5.2}$$

is fulfilled for all normal modes n considerably contributing to (2.4), the solution $\lambda_{a'a}(E)$ of (3.1) reads

$$\lambda_{a'a}(E) \doteq \frac{1}{2kT}\left(\frac{E}{S^{(1)}_{a'a}} - 1\right). \tag{5.3}$$

In this approximation the general expression (3.2) for the smooth overlap factor $\bar{\mathcal{R}}_{a'a}(E)$ reduces to its well-known classical form

$$\bar{\mathcal{R}}_{a'a}(E) \doteq \left[\pi\, 4kTS^{(1)}_{a'a}\right]^{-1/2} \exp\left[-\frac{(E - S^{(1)}_{a'a})^2}{4kTS^{(1)}_{a'a}}\right] = G(E - S^{(1)}_{a'a};\, 2kTS^{(1)}_{a'a}) \tag{5.4}$$

(see e.g. LAX [2], RICKAYZEN [3], PERLIN [5], CURIE [18]).

Correspondingly, if condition (5.2) is fulfilled for $|E| = |\mathcal{J}_{a'} - \mathcal{J}_a|$, the general expression (4.3) for nonradiative multiphonon transition rates $w_{Na'a}$ reduces simply to

$$w_{Na'a} \doteq \frac{2\pi}{\hbar}\left\{\left|A_{a'a} + \frac{\mathcal{J}_{a'} - \mathcal{J}_a}{s^{(1)}_{a'a}} B^{(0)}_{a'a}\right|^2 + 2kT\left(C^{(-1)}_{a'a} - \frac{|B^{(0)}_{a'a}|^2}{S^{(1)}_{a'a}}\right)\right\} \bar{\mathcal{R}}_{a'a}(\mathcal{J}_a - \mathcal{J}_{a'}) \tag{5.5}$$

with the (temperature-independent) transition-specific energy coefficients $A_{a'a} \equiv \equiv a_{Na'a} = \sum_n A_{na'a}$, $B^{(0)}_{a'a} \equiv b^{(0)}_{Na'a}(0) = \sum_n B_{na'a}$, $C^{(-1)}_{a'a} \equiv c^{(-1)}_{Na'a}(0) = \sum_n C_{na'a}$ and $S^{(1)}_{a'a} \equiv \equiv s^{(1)}_{Na'a}(0) = \sum_n S_{na'a}$ being connected by a Schwarz' type inequality $|B^{(0)}_{a'a}|^2 \leqq \leqq C^{(-1)}_{a'a} S^{(1)}_{a'a}$ (cf. [1]) and the overlap factor $\bar{\mathcal{R}}_{a'a}(\mathcal{J}_a - \mathcal{J}_{a'})$ in classical approximation (5.4). The latter can be written in the form

$$G(\mathcal{J}_a - \mathcal{J}_{a'} - S^{(1)}_{a'a};\, 2kTS^{(1)}_{a'a}) = \left[\pi\, 4kTS^{(1)}_{a'a}\right]^{-1/2} \exp\left[-\frac{U_{a'a}}{kT}\right] \tag{5.6}$$

with the classical excitation energy

$$0 \leqq U_{a'a} \equiv \frac{(\mathcal{J}_a - \mathcal{J}_{a'} - S^{(1)}_{a'a})^2}{4S^{(1)}_{a'a}} \tag{5.7}$$

(cf. KRIVOGLAZ [17], RICKAYZEN [3], PERLIN [5], SINYAVSKIY and KOVARSKIY [6]) for a nonradiative multiphonon transition $|a\rangle \to |a'\rangle$ of the electronic system which satisfies the symmetry relation

$$U_{aa'} + \mathcal{J}_{a'} = U_{a'a} + \mathcal{J}_a \tag{5.8}$$

following trivially from its definition (5.7).

5.2 Semiclassical approximation

For energies within the ranges

$$\varepsilon_n \frac{\big||E| - S^{(1)}_{a'a}\big|}{S^{(2)}_{a'a}} \ll 1 \tag{5.9}$$

the solution $\lambda_{a'a}(|E|)$ of eq. (3.1) reads, for arbitrary temperatures,

$$\lambda_{a'a}(|E|) \doteq \frac{|E| - S^{(1)}_{a'a}}{S^{(2)}_{a'a}} \tag{5.10}$$

so that the corresponding smooth overlap factor (3.2) equals approximately

$$\bar{\mathscr{R}}_{a'a}(E) \doteq [\pi\, 2S^{(2)}_{a'a}]^{-1/2} \exp\left[-\frac{(|E| - S^{(1)}_{a'a})^2}{2S^{(2)}_{a'a}} + \frac{E - |E|}{2kT}\right] = \tag{5.11}$$

$$= G(|E| - S^{(1)}_{a'a}; S^{(2)}_{a'a}) \exp\left[\frac{E - |E|}{2kT}\right].$$

This expression corresponds, for positive E, exactly to the well-known semiclassical overlap-factor expression (see e.g. LAX [2], RICKAYZEN [3], STASIW [4], PERLIN [5], CURIE [18], HAUG [19]) while, for negative E, it is modified so as to obey, at least, the fundamental symmetry relation (3.6) assuring detailed balance (4.7).

Correspondingly, if now the inequality (5.9) holds for $|E| = |\mathscr{J}_{a'} - \mathscr{J}_a|$, the general expression (4.3) for nonradiative multiphonon transition rates $w_{Na'a}$ reduces to

$$w_{Na'a} \doteq \frac{2\pi}{\hbar}\left\{\left|A_{a'a} + \frac{\mathscr{J}_{a'} - \mathscr{J}_a}{S^{(1)}_{a'a}} B^{(0)}_{a'a}\right|^2 + \left(C^{(0)}_{a'a} - \frac{|B^{(2)}_{a'a}|^2}{S^{(2)}_{a'a}}\right)\right\} \bar{\mathscr{R}}_{a'a}(\mathscr{J}_a - \mathscr{J}_{a'}) \tag{5.12}$$

(see in contrast to this RICKAYZEN [3]; cf. a somewhat less practicable expression given by HAUG [19]) with the temperature-dependent transition-specific quantities $B^{(1)}_{a'a} \equiv b^{(1)}_{Na'a}(0)$, $C^{(0)}_{a'a} \equiv c^{(0)}_{Na'a}(0)$ and $S^{(2)}_{a'a} \equiv s^{(2)}_{Na'a}(0)$ connected, again, by a Schwarz' type inequality $|B^{(1)}_{a'a}|^2 \leqq C^{(0)}_{a'a} S^{(2)}_{a'a}$.

The semiclassical expression attained by SINYAVSKIY and KOVARSKIY [6] (see also BONCH-BRUEVICH[7]) on the basis of the familiar adiabatic coupling scheme within the so-called Non-Condon approximation gives, in general, results of approximately the same order of magnitude as (5.12). Formally, it could be obtained from the latter by putting simply $A_{a'a} = 0$ and $B^{(m)}_{a'a} = 0$, $m = 0$ and 1, in (5.12).

5.3 Comparison with the exact solution

In applications, the distance $|\mathscr{J}_{a'} - \mathscr{J}_a|$ of the effective electronic levels involved is usually several times larger than the associated readjustment energy $S^{(1)}_{a'a}$ of the phonon field, $|\mathscr{J}_{a'} - \mathscr{J}_a| \approx 10^{1/2}.\, S^{(1)}_{a'a}$ (see e.g. PEKAR [10], RICKAYZEN [3], FOWLER

and DEXTER [20]). Hence, the formulae given in this section apply only at extremely high temperatures (and then, because of $S^{(2)}_{a'a} \doteq 2kTS^{(1)}_{a'a}$, the semiclassical approximation gives the same results as the classical one) whereas, at lower temperatures, the condition of validity of the semiclassical approximation usually is not fulfilled.

For a visualization of the deviations of the classical and semiclassical overlap-factor expressions from the corresponding exact one we consider the 1st – and 2nd-order derivatives (3.8) of the solution $\lambda_{a'a}(E)$ of eq. (3.1) which are $\lambda^{(1)}_{a'a}(E) > 0$ for any E and $\lambda^{(2)}_{a'a}(E) \lessgtr 0$ for $E \gtrless 0$ and, due to (3.8) and (3.12),

$$\lambda^{(1)}_{a'a}(\pm S^{(1)}_{a'a}) = \frac{1}{S^{(2)}_{a'a}} < \frac{1}{2kTS^{(1)}_{a'a}} < \frac{1}{S^{(2)}_{Na'a}\left(-\frac{1}{2kT}\right)} = \lambda^{(1)}_{a'a}(0) \tag{5.13}$$

at $E = \pm S^{(1)}_{a'a}$ and 0. Thus, in observing relation (3.4), we can draw for the exact solution $\lambda_{a'a}(E)$ of eq. (3.1) as compared with the approximate ones (5.3) and (5.10) generally the graph in fig. 1a from which, by integrating $\Phi^{(1)}_{a'a}(E) = -\lambda_{a'a}(E)$ (3.7) and observing $\Phi_{a'a}(\pm S^{(1)}_{a'a}) = (-1 \pm 1)(S^{(1)}_{a'a}/2kT)$, the graph in fig. 1b for the exact function $\Phi_{a'a}(E)$ (3.3) in the exponential in $\overline{\mathcal{R}}_{a'a}(E)$ (3.2) is obtained.

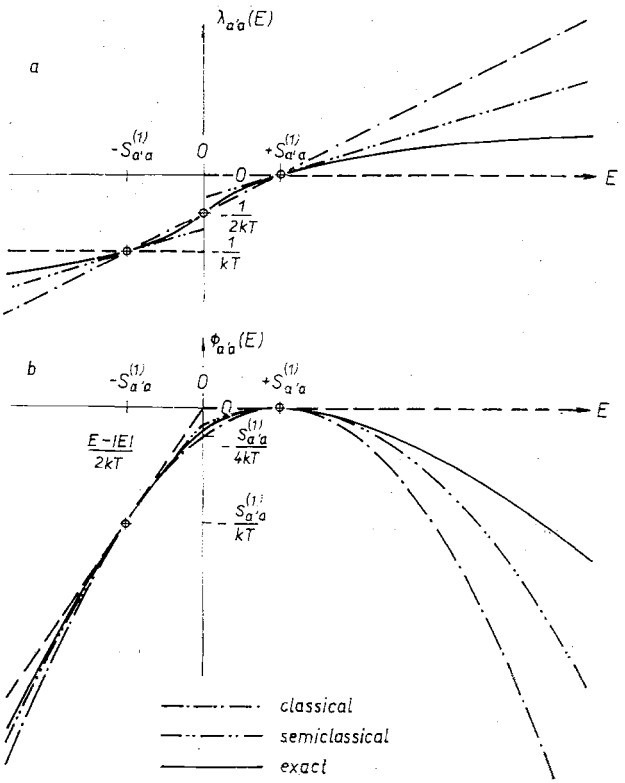

Fig. 1.

From the latter we see that in the energy ranges $|E| > S^{(1)}_{a'a}$ the value of the function $\Phi_{a'a}(E)$, decisive for the order of magnitude of the smooth overlap factor $\bar{\mathcal{R}}_{a'a}(E)$, is underestimated not only by the classical but, quite generally, by the semiclassical approximation too.

In performing corresponding exemplaric numerical calculations (which can be easily carried out, for the case of small phonon dispersion at least, on the basis of formulae (I.6.4) and (5.11)) we see that for typical values of the parameters involved the underestimation of the numerical value of the overlap factor (3.2) by the semiclassical formula (5.11) may change in general even its order of magnitude, this discrepancy growing extremely quickly with increasing energy $|E|$. This fact shows clearly that the use of the simple (and popular) overlap-factor formulae (5.4) or (5.11) should be urgently avoided in nonradiative multiphonon transition-rate calculations, unless conditions (5.2) or (5.9) are in fact fulfilled. Henceforth, the use of more straightforward overlap-factor formulae such as of the type (I.6.4) is stringently required.

6. SUPERIOR APPROXIMATIONS

On the basis of the concept of the transition-specific phonon energy $\varepsilon_{a'a}$ (2.13) being effective experimentally at medium temperatures, $kT \approx \varepsilon_{a'a}$, we shall derive in this section overlap-factor formulae which, independently of the largeness of phonon dispersion, account correctly for the skewness $\varrho^{(3)}_{a'a} = S^{(3)}_{a'a} = \varepsilon^2_{a'a} S^{(1)}_{a'a}$ (see (2.8) and (2.13)) of the overlap-factor curve (3.2). In making $\varepsilon_{a'a}$, at the same time, to serve as a temperature-independent "mean" phonon energy in a certain low-dispersion expansion (see in contrast to this [16] and [17]) for all the higher-order derivatives $S^{(m)}_{a'a}$ in (2.4), $m = 4, 5, \ldots$, the formulae obtained will, in the case of small phonon dispersion, automatically reduce to the single-phonon-energy formula (I.6.4) as it ought to be required from any approximation formula to be applied, eventually, in ranges of large energies $|E|$.

6.1 Effective-phonon-energy approximation

In order to calculate the function $s_{Na'a}(\lambda)$ (2.4) as well as its low-order derivatives $s^{(1)}_{Na'a}(\lambda)$ and $s^{(2)}_{Na'a}(\lambda)$ in (3.1) to (3.3) in the approximation just indicated we consider the temperature-independent moments

$$S'_{(m)a'a} \equiv \sum_n S_{na'a}(\varepsilon_n^2 - \varepsilon^2_{a'a})^m \tag{6.1}$$

of phonon dispersion, $m = 0, 1, 2, \ldots$, in terms of which the odd- and even-order derivatives (2.5) of $s_{Na'a}(\lambda)$ (2.4) at $\lambda = 0$ can be written as

$$S^{(2p+1)}_{a'a} = \sum_{m=0}^{p} \frac{p!}{m!(p-m)!} S'_{(m)a'a} \varepsilon^{2(p-m)}_{a'a} \tag{6.2a}$$

and

$$(6.2b)\qquad S_{a'a}^{(2p+2)} = 2kT\sum_{l=0}^{\infty}\frac{f^{(2l)}}{(2l)!}\left(\frac{1}{2kT}\right)^{2l}\sum_{m=0}^{p+l}\frac{(p+l)!}{m!\,(p+l-m)!}\,S'_{(m)a'a}\varepsilon_{a'a}^{2(p+l-m)},$$

respectively. In confining ourselves now to the 1st order which is, because of $S'_{(1)a'a} = 0$, equivalent to the 0th order of phonon dispersion we obtain (with $S'_{(0)a'a} = S_{a'a}^{(1)}$) approximately $S_{a'a}^{(2p+1)} \doteq \varepsilon_{a'a}^{2p} S_{a'a}^{(1)}$, $p = 2, 3, \ldots$, and $S_{a'a}^{(2p+2)} \doteq \varepsilon_{a'a}^{2p+1} S_{a'a}^{(1)} \coth(\varepsilon_{a'a}/2kT)$, $p = 0, 1, 2, \ldots$, for the derivatives $S_{a'a}^{(m)}$ (2.5) in (2.4).

In this approximation the solution $\lambda_{a'a}(E)$ of eq. (3.1) reads simply

$$(6.3)\qquad \lambda_{a'a}(E) \doteq \frac{1}{\varepsilon_{a'a}}\operatorname{arcsinh}\left(\frac{E}{S_{a'a}^{(1)}}\sinh\frac{\varepsilon_{a'a}}{2kT}\right) - \frac{1}{2kT}$$

from which follows for the overlap factor (3.2) immediately

$$(6.4)\qquad \bar{\mathcal{R}}_{a'a}(E) \doteq \frac{1}{\varepsilon_{a'a}}\left\{2\pi\frac{1}{\varepsilon_{a'a}}\left[\left(\frac{S_{a'a}^{(1)}}{\sinh\frac{\varepsilon_{a'a}}{2kT}}\right)^2 + E^2\right]^{1/2}\right\}^{-1/2}\cdot$$

$$\cdot\exp\left\{\frac{1}{\varepsilon_{a'a}}\left[\left(\frac{S_{a'a}^{(1)}}{\sinh\frac{\varepsilon_{a'a}}{2kT}}\right)^2 + E^2\right]^{1/2} - \frac{S_{a'a}^{(1)}}{\varepsilon_{a'a}}\coth\frac{\varepsilon_{a'a}}{2kT} - \right.$$

$$\left. - \frac{E}{\varepsilon_{a'a}}\operatorname{arcsinh}\left(\frac{E}{S_{a'a}^{(1)}}\sinh\frac{\varepsilon_{a'a}}{2kT}\right) + \frac{E}{2kT}\right\}.$$

6.2 Modified effective-phonon-energy approximation

In order to derive an explicit overlap-factor formula superior, for $|E| \approx (10^0 \ldots 10^1)\cdot S_{a'a}^{(1)}$, to all the other ones given so far we consider the temperature-dependent moments

$$(6.5)\qquad S''_{(m)a'a} \equiv \sum_n \varepsilon_n S_{na'a}\coth\frac{\varepsilon_n}{2kT}\,(\varepsilon_n^2 - \varepsilon_{a'a}^2)^m$$

in terms of which the even-order derivatives $S_{a'a}^{(2p+2)}$ (2.5b) in (2.4) can be written as

$$(6.6)\qquad S_{a'a}^{(2p+2)} = \sum_{m=0}^{p}\frac{p!}{m!\,(p-m)!}\,S''_{(m)a'a}\varepsilon_{a'a}^{2(p-m)}.$$

Thus, we have now (with $S''_{(0)a'a} = S_{a'a}^{(2)}$) in 0th order of phonon dispersion approximately $S_{a'a}^{(2p+2)} \doteq \varepsilon_{a'a}^{2p} S_{a'a}^{(2)}$, $p = 1, 2, \ldots$.

The latter modification of the procedure presented in the preceding subsection leads to the expression

$$\lambda_{a'a}(|E|) \doteq \frac{1}{\varepsilon_{a'a}} \ln \frac{|E| + \left[\left(\frac{S^{(2)}_{a'a}}{\varepsilon_{a'a}}\right)^2 - (S^{(1)}_{a'a})^2 + E^2\right]^{1/2}}{S^{(1)}_{a'a} + \frac{S^{(2)}_{a'a}}{\varepsilon_{a'a}}} \tag{6.7}$$

for the approximate solution of eq. (3.1) from which we get in accordance with symmetry relation (3.6) for the overlap factor (3.2) now

$$\begin{aligned} \bar{\mathscr{R}}_{a'a}(E) \doteq \frac{1}{\varepsilon_{a'a}} \Bigg\{ 2\pi \frac{1}{\varepsilon_{a'a}} \left[\left(\frac{S^{(2)}_{a'a}}{\varepsilon_{a'a}}\right)^2 - (S^{(1)}_{a'a})^2 + E^2\right]^{1/2} \Bigg\}^{-1/2} \\ \cdot \exp \Bigg\{ \frac{1}{\varepsilon_{a'a}} \left[\left(\frac{S^{(2)}_{a'a}}{\varepsilon_{a'a}}\right)^2 - (S^{(1)}_{a'a})^2 + E^2\right]^{1/2} - \frac{S^{(2)}_{a'a}}{\varepsilon^2_{a'a}} - \\ - \frac{|E|}{\varepsilon_{a'a}} \ln \frac{|E| + \left[\left(\frac{S^{(2)}_{a'a}}{\varepsilon_{a'a}}\right)^2 - (S^{(1)}_{a'a})^2 + E^2\right]^{1/2}}{S^{(1)}_{a'a} + \frac{S^{(2)}_{a'a}}{\varepsilon_{a'a}}} + \frac{E - |E|}{2kT} \Bigg\}. \end{aligned} \tag{6.8}$$

6.3 Discussion

In examining the gentleness of the approximate overlap-factor expressions (6.4) and (6.8) we satisfy ourselves first of all that for small phonon dispersion, i.e. when $\varepsilon_n \to \varepsilon_0$ with a nearly common phonon energy ε_0 so that we have $\varepsilon_{a'a}$ (2.13) $\to \varepsilon_0$ and $S^{(2)}_{a'a}$ (6.6) $\to \varepsilon_0 S^{(1)}_{a'a} \coth(\varepsilon_0/2kT)$, both formulae become identical to one another and reduce to the corresponding smoothed single-phonon-energy formula (I.6.4) as required.

Returning now to the case of large phonon dispersion, we easily verify by expanding the exponential function in (6.8) into a Taylor series that the low-order ($|E| - S^{(1)}_{a'a}$) – powers, inclusive the cubic one (cf. also KRIVOGLAZ and PEKAR [16], STASIW [4], PERLIN [5]), of the exact exponential function in (3.9) are reproduced correctly by (6.8). From this follows that the modified effective-phonon-energy formula (6.8) is, any way, superior to the semiclassical one (5.11) and can be, henceforth, applied in a correspondingly larger energy range.

To get an idea about the magnitude of the latter we recall that the approximation made in subsection 6.2 is of such a special kind that the low-order derivatives $S^{(1)}_{a'a}$, $S^{(2)}_{a'a}$ and $S^{(3)}_{a'a}$ (2.5) in $s_{Na'a}(\lambda)$ (2.4) are left untouched hereby. Thus, because of the fast convergence of the expansion (2.4) (see KRIVOGLAZ [17]), the functional value of the

solution $\lambda_{a'a}(|E|)$ of eq. (3.1) as well as that of the function $\Phi_{a'a}(|E|)$ in (3.2) can be considered to be nearly unaltered by this procedure for $\lambda_{a'a}(|E|)$-values up to an order of $\varepsilon_{a'a}\,\lambda_{a'a}(|E|) \approx 10^0$. These values correspond at low temperatures, where we have $\varepsilon_{a'a}\,\lambda_{a'a}(|E|) \approx \ln(|E|/S^{(1)}_{a'a})$ (according to (6.7) and (2.5)), just to energies of the order $|E| \approx 10^{1/2}$. $S^{(1)}_{a'a}$ being of actual interest in typical nonradiative multiphonon band-imperfection transitions in semiconductors (which are indeed capable of dominating the associated radiative ones, see [21]).

Since, beyond this, the deviations of (6.8) from (3.2) are even decreasing with increasing temperature, due to improving convergence of (2.4), expression (6.8) may be in fact considered to be a very gentle explicit overlap-factor formula enabling in connection with (6.7) and (4.3), at arbitrary temperatures, reliable numerical calculations of nonradiative multiphonon transition rates.

At medium and high temperatures which are of most interest in practice we get from (2.6) simply $S^{(2)}_{a'a} \doteq \varepsilon_{a'a} S^{(1)}_{a'a} \coth(\varepsilon_{a'a}/2kT)$ so that the modified effective-phonon-energy formula (6.8) reduces, for arbitrarily large phonon dispersion, to the original effective-phonon-energy formula (6.4) again.

7. CONCLUSION

For a somewhat idealized phonon system, a study of a number of relevant mathematical aspects of nonradiative multiphonon transition-rate calculations within the framework of the static coupling scheme has been performed in this paper. The idealization was connected with the severe restrictions that, firstly, the normal modes were strictly harmonic and, secondly, the electron-phonon interaction was linear in the normal coordinates. If these conditions are not well fulfilled which may be considered to be generally the case in molecules (see e.g. SCHLAG, SCHNEIDER and FISCHER [22]) as well as for strongly localized imperfection electrons coupled with associated local modes in semiconductors (see e.g. FOWLER and DEXTER [20]), a generalization of the transition-rate calculations starting directly from the more general expression (I.2.9) given in [1] is required, in close analogy to that presented by KUBO and TOYOZAWA [8] within the framework of the adiabatic coupling scheme. The formulae obtained will then, in particular, account for the temperature-induced shift of the center of gravity of the luminescense band (cf. O'ROURKE [23], MCCUMBER [9], HAUG [19]) which is frequently observed experimentally (see e.g. MEYER [13], DEXTER [14]) as well as lead to a certain modification of the functional behaviour of the overlap-factor curve on the high-energy wing which may alter, more or less significantly (cf. also [22]), the probabilities of nonradiative multiphonon transitions.

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References

[1] PÄSSLER R., Czech. J. Phys. *B 24* (1974), 322.
[2] LAX M., J. Chem. Phys. *20* (1952), 1752.
[3] RICKAYZEN G., Proc. Roy. Soc. *A 241* (1957), 480.
[4] STASIW O., Elektronen- und Ionenprozesse in Ionenkristallen. Springer, Berlin—Göttingen—Heidelberg, 1959.
[5] PERLIN YU. E., UFN *80* (1963), 553.
[6] SINYAVSKIY E. P., KOVARSKIY V. A., FTT *9* (1967), 1464.
[7] BONCH-BRUEVICH V. L., Vestn. Univ. Moskva (III) *12*, Nr. 5, (1971), 586.
[8] KUBO R., TOYOZAWA Y., Progr. theor. Phys. *13* (1955), 160.
[9] MCCUMBER D. E., J. math. Phys. *5* (1964), 221.
[10] PEKAR S. I., UFN *50* (1953), 197.
[11] KUBO R., *in* "Halbleiter und Phosphore", Akademie-Verlag Berlin, 1958, p. 584.
[12] HUANG K., RHYS A., Proc. Roy. Soc. *A 204* (1950), 406.
[13] MEYER H. J. G., Halbleiterprobleme *III* (1956), 230.
[14] DEXTER D. L., Solid State Phys. *6* (1958), 353.
[15] HOWGATE D. W., Phys. Rev. (2) *177* (1969), 1358.
[16] KRIVOGLAZ M. A., PEKAR S. I., Trudy Inst. Fiz. AN USSR *4* (1953), 37.
[17] KRIVOGLAZ M. A., ZhETF *25* (1953), 191.
[18] CURIE D., Luminescence cristalline, Paris, 1960.
[19] HAUG A., Theoretische Festkörperphysik II, Deuticke, Wien, 1970.
[20] FOWLER W. B., DEXTER D. L., Phys. Rev. (2) *128* (1962), 2154.
[21] PÄSSLER R., phys. stat. sol. (b) *65* (1974), 561.
[22] SCHLAG E. W., SCHNEIDER E., FISCHER S. F., Ann. Rev. Phys. Chem. *22* (1971), 465.
[23] O'ROURKE R. C., Phys. Rev. *91* (1953), 265.