SOVIET PHYSICS JETP VOLUME 17, NUMBER 2 AUGUST, 1963

TEMPERATURE DEPENDENCE OF OPTICAL AND NONRADIATIVE TRANSITIONS IN SEMICONDUCTORS

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Submitted to JETP editor September 12, 1962

J. Exptl. Theoret. Phys. (U.S.S.R.), 44, 703-709 (February, 1963)

A differential-difference equation is written for the probability of some optical and nonradiative transitions in semiconductors. The appropriate expression at T = 0 is taken as the "initial" function. In a number of cases approximate solutions of the obtained equation are successfully found. Under certain assumptions the equation transforms into the diffusion equation and is solved exactly. Hence, the proposed method permits the construction of the investigated expression $J_W(E;T)$ by means of its values at T = 0.

1. Optical transitions of localized electrons in semiconductors were studied by many authors[1-5]. The process was analyzed in the adiabatic approximation: if the lattice part of the wave function of the system is denoted by $\Phi_{s_j l_j}(\mathbf{R})$, where s_j is the set of quantum numbers characterizing the state of the fast subsystem and l_j the quantum numbers of the lattice, then the cross sections of the transitions from the state s_1 to the state s_2 are described by expressions of the form:

$$J_W(E;T) = \sum_{l_1, l_2} p_{l_1} |(\Phi_{s_1 l_1}(\mathbf{R}),\ W(\mathbf{R})\,\Phi_{s_2 l_2}(\mathbf{R}))|^2$$

$$\times\ \delta(E - [E_{s_2 l_2} - E_{s_1 l_1}]);$$

$$p_{l_1} = \exp(-E_{s_1 l_1}\beta)\Big[\sum_{l_1'} \exp(-E_{s_1 l_1}\beta)\Big]^{-1}, \qquad \beta = 1/kT, \quad (1)$$

where $E_{s_j l_j}$ is the total system energy (the total wave function of the system is $\varphi_{s_j}(\mathbf{r}, \mathbf{R})\,\Phi_{s_j l_j}(\mathbf{R})$).

A computation of the cross-sections of nonradiative capture of electronic excitations of molecular crystals by impurity molecules[6-8] leads to expressions of the form (1), as do a number of other problems associated with the electronic excitations of molecular crystals.

$$W(\mathbf{R}) = \int \varphi^*_{s_2}(\mathbf{r}, \mathbf{R})\, e\mathbf{r}\, \varphi_{s_1}(\mathbf{r}, \mathbf{R})\, d\mathbf{r}$$

is the dipole moment matrix element which, as a rule, depends weakly on **R**, so that the assumption $W(\mathbf{R}) = \text{const}$, made in[2-5], is usually sufficiently justified. For the nonradiative capture process $W(\mathbf{R})$ is a certain scalar function whose dependence on R can be essential.

Let us consider the lattice vibrations to be harmonic, i.e., the adiabatic potential in the state s_1 equals

$$U_1(\mathbf{R}) = \tfrac{1}{2}(\mathbf{R} - \mathbf{R}_1)\,\Omega_1^2\,(\mathbf{R} - \mathbf{R}_1),$$

and in the state s_2

$$U_2(\mathbf{R}) = \tfrac{1}{2}(\mathbf{R} - \mathbf{R}_2)\,\Omega_2^2\,(\mathbf{R} - \mathbf{R}_2) + E_0,$$

where the N-dimensional tensor and vector Ω_j and $\mathbf{R}_j$ describe the elastic properties and equilibrium of the lattice configuration, respectively.

If $\mathbf{R}_1 = \mathbf{R}_2$, $\Omega_1^2 = \Omega_2^2$ and $W(\mathbf{R}) = \text{const}$, then $J_W(E;T)$ is proportional to $\delta(E - E_0)$; hence, the quantities $\mathbf{\Lambda} = \mathbf{R}_2 = \mathbf{R}_1$ and $\Gamma = \Omega_2^2 - \Omega_1^2$ and the dependence $W(\mathbf{R})$ on **R** specify the diffusion of $J_W(E;T)$. Since writing $J_W(E;T)$ in (1) does not, in practice, yield any information on the behavior of $J_W(E;T)$ as a function of E and T, the purpose of a whole series of researches[2-8] was to select an approximation and to construct as simple analytic expressions for $J_W(E;T)$ as possible.

If Ω_1^2 and Ω_2^2 have no local frequencies, then the approximation $\Gamma = 0$ used in[2-4] is satisfactory. By assuming also $W(\mathbf{R}) = \text{const}$, Pekar[2] and Huang and Rhys[3] obtained an exact expression for $J_W(E;T)$ only in the very particular case when all the normal lattice vibrations actively taking part in the transition have the same frequency. For the case of arbitrary dispersion, an approximate expression was obtained in[4] for $J_W(E;T)$, valid in a certain neighborhood

$$\overline{E} = \int_{-\infty}^{\infty} E J_W(E;T)\, dE$$

and for sufficiently strong coupling of the fast subsystem to the lattice. This latter means that the half-width of $J_W(E; T)$ must be considerably greater than a certain mean energy of the normal vibrations actively taking part in the transition. Ratner and Zil'berman [5] obtained approximate expressions for $J_W(E; T)$ in the case $\Lambda \neq 0$, $\Gamma \neq 0$, and $W(\mathbf{R}) = \text{const}$.

We propose here a new approach to the study of $J_W(E; T)$, which will permit a more graphic tracing of the temperature dependence in a number of cases and which avoids certain assumptions used in previous work [2-8]. This method consists of the construction of an equation which $J_W(E; T)$ satisfies and of finding its solutions; this will afford the possibility of constructing $J_W(E; T)$ if the form of $J_W(E; T_0)$ is known for some temperature $T_0 < T$. The case $\Lambda \neq 0$, $\Gamma = 0$, and $W(\mathbf{R}) = \text{const}$ is examined in detail in this paper; only certain remarks are made with respect to analogous constructions for $\Gamma \neq 0$ and when taking account of the dependence of $W(\mathbf{R})$ on $\mathbf{R}$.

2. If $\Gamma = 0$ and $W(\mathbf{R}) = W(\mathbf{R}_0) = \text{const}$, then from the formulas obtained by Kubo and Toyozawa [1] we have

$$F(E;T) = \frac{1}{|W(\mathbf{R}_0)|^2} J_W(E;T) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \exp\Big\{i\Big[(E-E_0)\lambda - \sum a_k \sin\varepsilon_k\lambda\Big] + \sum a_k(2n_k+1)(\cos\varepsilon_k\lambda - 1)\Big\}\,d\lambda, \tag{2}$$

where $a_k = \omega_k\Lambda_k/2\hbar$ are nondimensional quantities, $\{\Lambda_k\}$ are the components of the vector $\mathbf{\Lambda}$ in the basis of the eigenvectors Ω, $\{\omega_k\}$ is the spectrum of the normal lattice vibrations, $\varepsilon_k = \hbar\omega_k$, and $n_k = [\exp(\varepsilon_k\beta) - 1]^{-1}$.

The representation (2) enables us to write for $F(E; T)$ the following differential-difference equation

$$\frac{\partial F(E;T)}{\partial T} = \frac{1}{2T}\sum \frac{a_k}{2}\,\frac{\beta\varepsilon_k}{\mathrm{sh}^2(\beta\varepsilon_k/2)}\,\Delta_k^2 F(E;T), \tag{3*}$$

where

$$\Delta_k^2 F(E;T) = F(E+\varepsilon_k;T) - 2F(E;T) + F(E-\varepsilon_k;T).$$

Hence, $\partial F(E'; T)/\partial T$ is related to the values of $F(E: T)$ only in a small neighborhood of E'. The function $F(E; T_0)$ with arbitrary T_0 can be selected as the "initial" distribution for (3), but for convenience in what follows we shall consider $T_0 = 0$ (see the Appendix).

If the interaction with the acoustic lattice vibrations can be neglected, then one term, corresponding to the minimum value of the $\{\varepsilon_k\}$ participating in the process, ε_0, plays a part in the right side of (3) at sufficiently low temperatures. The energy ε_0 corresponds either to the optical branch of the vibrations, within which we neglect the dispersion, or to a local vibration, i.e.,

$$\frac{\partial F(E;T)}{\partial T} = \frac{1}{2T}a_0\frac{\beta\varepsilon_0/2}{\mathrm{sh}^2(\beta\varepsilon_0/2)}\,\Delta_0^2 F(E;T). \tag{4}$$

Using the recursion relations for the Bessel functions of imaginary argument, an exact solution of (4) can be obtained if the form of $F(E; 0)$ is known:

$$F(E;T) = e^{-2a_0n_0}\sum_{l=-\infty}^{\infty} F(E+l\varepsilon_0;0)\,I_l(2a_0n_0). \tag{5}$$

Only those components for which $E + l\varepsilon_0 \geq E_0$ figure in the sum (5), since it is evident that $F(E; 0) = 0$ for $E < E_0$.

For limiting low temperatures we have from (5)

$$F(E;T) = F(E;0) + a_0e^{-\beta\varepsilon_0}\Delta_0^2 F(E;0). \tag{6}$$

If $\varepsilon_k = \varepsilon_0 = \text{const}$, Eq. (4) is valid for arbitrary temperature and

$$F(E;0) = e^{-a_0}\sum_{l=0}^{\infty}\frac{a_0^l}{l!}\,\delta(E-E_0-l\varepsilon_0), \tag{7}$$

where $a_0 = \Sigma a_k$.

The expression for $F(E; T)$ obtained by substituting (7) into (5) can be reduced by using the Lommel expansion [9] to the form

$$F(E;T) = \exp\Big[-a_0(2n_0+1) + \frac{\beta(E-E_0)}{2}\Big] \times \sum_{l=-\infty}^{\infty} I_l\big(2a_0\sqrt{n_0(n_0+1)}\big)\,\delta(E-E_0-l\varepsilon_0), \tag{8}$$

which agrees with the results of Pekar [2] and Huang and Rhys [3].

In many problems the case when $\Sigma a_k \gg 1$, i.e., when the half-width of $F(E; 0)$ is considerably greater than the energy of the normal vibrations actively taking part in the transition, a case examined by a number of authors [4,5], is realized. A good approximation for this case is

$$\Delta_k^2 F(E;T) = \varepsilon_k^2\,\partial^2 F(E;T)/\partial E^2, \tag{9}$$

where the error due to such a substitution diminishes as the temperature rises, i.e., as $F(E; T)$ diffuses.

Let us introduce instead of T a new independent variable $\tau(T) = \Sigma a_k\varepsilon_k^2 n_k$, which has a very graphic physical meaning: $2\tau(T)$ is the difference between the squares of the half-widths of $F(E; T)$ and $F(E; 0)$. Then, taking (9) into account, Eq.

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*sh = sinh.

(3) assumes the form:

$$\partial\tilde{F}(E;\,T)/\partial\tau = \partial^2\tilde{F}(E;\,T)/\partial E^2, \tag{10}$$

where $\tilde{F}(E;\,T)$ will henceforth denote the solution of (10) for $E\epsilon(-\infty,\,\infty)$ with the initial condition $\tilde{F}(E;\,0) = F(E;\,0)$. Since $\tau(0) = 0$, $F(E;\,0)$ determines $\tilde{F}(E;\,T)$ completely as a function of E and τ:

$$\tilde{F}(E;\,T) = \frac{1}{2\sqrt{\pi\tau}}\int\limits_{-\infty}^{\infty} e^{-(E-x)^2/4\tau}F(x;\,0)\,dx; \tag{11}$$

$\tau(T)$ is a monotonically increasing function of T, hence the following conclusions can be drawn on the behavior of $\tilde{F}(E:\,T)$, based only on the general properties of the solution of the diffusion equation such as the principles of the maximum and minimum values. Moreover, the signs of $\partial\tilde{F}(E;\,T)/\partial T$ and $\partial\tilde{F}(E:\,T)/\partial\tau$ agree, i.e., the sign of $\partial\tilde{F}(E:\,T)/\partial T$ is determined by the dependence of $\tilde{F}(E:\,T)$ on τ, which can be obtained from (11) by using a sufficiently graphic picture of one dimensional diffusion with a constant diffusion coefficient. The latter considerations permit a qualitative explanation of the Lyons-White effect[10].

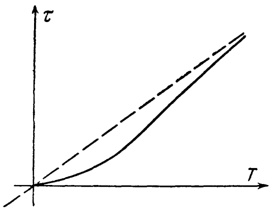
However, for quantitative computations knowledge of the dependence of τ on T is required. The character of the dependence $\tau(T)$ is shown in the sketch. At low temperatures, according to[11],

$$\tau(T) = \alpha T^4, \tag{12}$$

where $\alpha > 0$ is independent of the temperature. For $kT \gg \varepsilon_k$

$$\tau(T) = k(\overline{E} - E_0)T, \tag{13}$$

where $\overline{E} - E_0$ can be measured directly and furthermore at any temperature, since $d\overline{E}/dT = 0$ in the case under consideration.



If the acoustic lattice vibrations play a noticeable part in the transition, then for sufficiently low temperatures terms corresponding to the lowest ε_k should be retained in the right side of (3), i.e., the condition $\Sigma a_k \gg 1$ is not necessary for the correctness of (10) in this case. Taking account of (12), we have

$$\tilde{F}(E;\,T) = \frac{1}{2\sqrt{\pi\alpha T^4}}\int\limits_{E_0}^{\infty} e^{-(E-x)^2/4\alpha T^4}F(x;\,0)\,dx. \tag{14}$$

Since the half-width of the fundamental solution (10) is considerably less than the half-width of $F(E:\,0)$ at sufficiently low temperatures, $F(x;\,0)$ under the integral sign can be expanded in a Taylor series about x = E. In the first approximation

$$\tilde{F}(E;\,T) = F(E;\,0) + \alpha T^4\partial^2F(E;\,0)/\partial E^2. \tag{15}$$

Let us compare the approximate expression (11) with the exact expression of $F(E;\,T)$. If we start from the exact expression for $F(E;\,0)$

$$F(E;\,0) = \exp\left(-\sum a_k\right)\frac{1}{2\pi}\int\limits_{-\infty}^{\infty}\exp\left\{i(E-E_0)\lambda + \sum a_k e^{-i\varepsilon_k\lambda}\right\}d\lambda, \tag{16}$$

then by using (11) it can be shown that for all temperatures

$$M_0 = \int\limits_{-\infty}^{\infty}\tilde{F}(E;\,T)\,dE = \int\limits_{-\infty}^{\infty}F(E;\,T)\,dE = 1,$$

$$M_l = \int\limits_{-\infty}^{\infty}(E-\overline{E})^l\tilde{F}(E;\,T)\,dE = \int\limits_{-\infty}^{\infty}(E-\overline{E})^l F(E;\,T)\,dE$$

for $l = 2$ and $l = 2s + 1$ $(s = 0,\,1,\,2,\ldots)$, where

$$\overline{E} = \int\limits_{-\infty}^{\infty}E\tilde{F}(E;\,T)\,dE = \int\limits_{-\infty}^{\infty}EF(E;\,T)\,dE.$$

For the remaining values of l the ratios of the corresponding moments of $F(E;\,T)$ and $\tilde{F}(E;\,T)$ tend exponentially to unity as the temperature is lowered.

If the coupling between the fast subsystem to the lattice is strong, i.e., $\Sigma a_k \gg 1$, then, as shown by Pekar and Krivoglaz[4], only the M_l with $l = 2$ and sometimes with $l = 3$ are essential in a certain not too large neighborhood of $\overline{E}$. As the temperature rises, the size of this neighborhood grows and the part of M_l with $l > 2$ decreases, i.e., $F(E;\,T)$ tends to a Gaussian curve, as follows also from general considerations.

We carried out a numerical computation of $F(E;\,T)$ and $\tilde{F}(E;\,T)$ in the dispersionless case. It seems that for F-centers in KBr (according to the results of Huang and Rhys[3] in this case $\Sigma a_k = 22.4$ and $\varepsilon_0 = 2 \times 10^{-2}$ eV) the error in replacing $F(E;\,T)$ by $\tilde{F}(E;\,T)$ for all T and a sufficiently large interval E did not exceed 2%, i.e., was almost within the limits of computational accuracy.

3. Leaving the discussion of the details to a subsequent paper, let us present certain results for the cases when $\Gamma \neq 0$ and the dependence of $W(\mathbf{R})$ on $\mathbf{R}$ is essential.

If $\Lambda \neq 0$, $\Gamma \neq 0$, $W(\mathbf{R}) = \text{const}$, then a Fokker-Planck equation of the form

$$\frac{\partial J_W(E;\, T)}{\partial T} = A(T)\frac{\partial^2 J_W(E;\, T)}{\partial E^2} + B(T)\frac{\partial J_W(E;\, T)}{\partial E}, \quad (17)$$

for which the behavior of the solution has been studied in detail [12], can be written for $J_W(E;\, T)$ in a first approximation in Γ. In contrast to the $\Gamma = 0$ case, the quantity $\overline{E}$ depends on the temperature, as is certain from the second term on the right side of the equation. The area under $J_W(E;\, T)$ is independent of the temperature, exactly as in the $\Gamma = 0$ case.

If the dependence of $W(\mathbf{R})$ on $\mathbf{R}$ is taken into account in the first approximation, i.e., if it is considered that

$$W(\mathbf{R}) = W(\mathbf{R}_0) + (\mathbf{R} - \mathbf{R}_0)\,\text{grad}\, W(\mathbf{R}_0),$$

then it can be shown that in the $\Lambda \neq 0$, $\Gamma = 0$ case the quantity J_W is expressed linearly in terms of the expressions considered in the preceding section

$$F(E;\, T), \qquad F(E \pm \varepsilon_m;\, T), \qquad F(E \pm \varepsilon_m \pm \varepsilon_l;\, T).$$

Let us note that in the weak coupling case, i.e., for $\Sigma a_k \ll 1$, terms containing $F(E \pm \varepsilon_m \pm \varepsilon_l;\, T)$ can be neglected in the expressions for $J_W(E;\, T)$. At sufficiently high temperatures, when owing to diffusion of $F(E;\, T)$ the difference in the values of $F(E;\, T)$, $F(E \pm \varepsilon_m;\, T)$, and $F(E \pm \varepsilon_m \pm \varepsilon_l;\, T)$ is insignificant, $J_W(E\colon T)$ is proportional to $F(E;\, T)$ with a proportionality coefficient dependent on the temperature. In contrast to the cases worked out above, the area under $J_W(E;\, T)$ depends on the temperature, hence the change in the area under $J_W(E\colon T)$ due to the change in the temperature can serve as a criterion of systems for which the dependence of $W(\mathbf{R})$ on $\mathbf{R}$ is essential. This case must be observed most clearly in systems with weak coupling of the fast subsystem to the lattice.

The author is deeply grateful to Corr. member I. M. Lifshitz of the U.S.S.R. Academy of Sciences for constant attention to the research and for valuable comments, and also to M. A. Krivoglaz for discussions of certain results.

APPENDIX

Let us discuss the behavior of $F(E;\, T)$ as a function of $\{a_k\}$ and $\{\varepsilon_k\}$. The equation

$$\partial F(E;\, 0)/\partial a_k = F(E - \varepsilon_k;\, 0) - F(E;\, 0) \qquad (A.1)$$

can be written for $F(E;\, 0)$ by using the representation (16). Since we have $F(E\colon 0) = \delta(E - E_0)$ for $\{a_k\} = \{0\}$, we write

$$F(E;\, 0) = \exp\left(-\sum a_k\right)\sum_{\mathbf{l}}\prod_{i=1}^{N}\frac{(a_i)^{l_i}}{l_i!}\,\delta\left(E - E_0 - \sum l_i\varepsilon_i\right), \qquad (A.2)$$

where $\mathbf{l}$ is an integer N-dimensional vector with non-negative components. Writing $F(E;\, 0)$ in the form (A.2) can be useful if the transition is effective only through the optical branches of the normal vibrations, within which the dispersion can be neglected (local vibrations can be present instead of the optical branches). Hence, only a few terms in (A.2) are different from zero and in certain particular cases a simple exact expression for $F(E;\, 0)$ can be obtained.

Since no such construction has been made before [1-4] for $\varepsilon_k \neq \text{const}$, let us present the result of a computation for the simplest case when the transition is accomplished because of two optical branches. If $\varepsilon_1 = 2\varepsilon_2$, then

$$F(E;\, 0) = e^{-(a_1+a_2)}\sum_{p=0}^{\infty}\frac{(-a_1)^{p/2}}{p!}H_p\left(i\frac{a_2}{2\sqrt{a_1}}\right)\delta(E - E_0 - p\varepsilon_2), \qquad (A.3)$$

where $H_p(z)$ is the Hermite polynomial and $a_1 = \Sigma a_{k_1}$; the sum is taken over such k_1 that $\varepsilon_{k_1} = \varepsilon_1$; $a_2 = \Sigma a_{k_2}$ for $\varepsilon_{k_2} = \varepsilon_2$.

In conclusion let us indicate the possibility, in principle, of measuring certain of the quantities $\{a_k\}$. Let us introduce for the acoustic vibrations a density a_k, in the energy interval $\gamma f(\varepsilon)$, i.e.,

$$\sum a_{k'} = \gamma\int_0^{\varepsilon_a} f(\varepsilon)\, d\varepsilon,$$

where k' enumerates the acoustic vibrations, γ characterizes the coupling force between the acoustic vibrations and the fast subsystem, and ε_a is the energy corresponding to the ceiling of the acoustic zone. Hence

$$\frac{\partial F(E;\, 0)}{\partial\gamma} = \int_0^{\varepsilon_a} f(\varepsilon)F(E - \varepsilon;\, 0)\, d\varepsilon - F(E;\, 0)\int_0^{\varepsilon_a} f(\varepsilon)\, d\varepsilon. \qquad (A.4)$$

Let the part of the acoustic vibrations in the transition process be small, i.e., $\gamma \ll 1$. Expanding $F(E;\, 0)$ in powers of γ, we have in first approximation

$$F(E;\, 0) = F(E;\, 0)\big|_{\gamma=0}\left(1 - \gamma\int_0^{\varepsilon_a} f(\varepsilon)\, d\varepsilon\right) + \gamma\int_0^{\varepsilon_a} f(\varepsilon)F(E - \varepsilon;\, 0)\big|_{\gamma=0}\, d\varepsilon. \qquad (A.5)$$

Since the spacing between the longest wavelength peak $F(E;\, 0)\big|_{\gamma=0}$ corresponding to $E = E_0$ and its closest peak equals the least of the energies of the optical and local vibrations that take active part in the process, i.e., greater than ε_a, we have from (A.5) and (A.2) for E in the interval $(E_0, E_0 + \varepsilon_a)$

$$F(E; 0) = \exp\left(-\sum_{k \neq k'} a_k\right)\left[\left(1 - \gamma \int_0^{\varepsilon_a} f(\varepsilon)\, d\varepsilon\right) \times \delta(E - E_0) + \gamma f(E - E_0)\right]. \qquad (A.6)$$

Analogous "satellites" but with different factors for $\gamma f(\varepsilon)$ appear on the short wavelength side of each peak $F(E: 0)|_{\gamma=0}$. Hence the density $a_{k'}$ in the energy interval can be found in this case from the form of the absorption spectrum.

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Translated by M. D. Friedman
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