Theory of the multiphonon capture of an electron by a deep trapping center

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It is shown that the multiphonon capture of an electron by a deep center is governed over a wide temperature range by thermally activated tunneling. The capture cross section is calculated in the model of a "zero-radius" center interacting with a single mode of local vibrations. The results agree with experiment in terms of both the value of the cross section and its temperature dependence. An applicability criterion is obtained for the "zero-radius potential" model.

The capture of a free electron by a deep center in a crystal should liberate an amount of energy at least equal to the binding energy ε_T of the electron at the center. In a number of cases it can be assumed that this energy is given up to lattice vibrations.[1] If $\varepsilon_T \gg \hbar\omega$, where ω is the vibrational frequency, one speaks of multiphonon capture. Underlying any treatment of multiphonon transitions in the concept of adiabatic potentials (terms) for the motion of the nuclei. For simplicity we assume that the leading role in the formation of the terms is played by a single mode of local vibrations. Then one can describe the transition with the aid of the configuration diagram illustrated in Fig. 1. Here the terms $U_1(x)$ and $U_2(x)$, corresponding to bound and free electron states, touch at the point x_c. (We shall call the configurational coordinate x the "nuclear coordinate".) The touching, rather than intersection, of the curves is a general circumstance. At the point x_c the electron binding energy $\varepsilon(x) = U_2(x) - U_1(x)$ goes to zero, and the electronic level goes into the continuum. It is known[2] that near this point $\varepsilon(x) \propto (x - x_c)^2$, corresponding to a touching of the curves. This means that in a parabolic approximation the potentials $U_1(x)$ and $U_2(x)$ correspond to different frequencies. Nevertheless, in the standard model usually used to study multiphonon capture $U_1(x)$ and $U_2(x)$ are represented by identical parabolas displaced relative to each other (here the curves do not touch but intersect). This model has the attractive feature that the overlap integral of the vibrational wave functions, which determines the leading exponential dependence of the transition probability on the parameters of the problem, can be evaluated exactly.[3] We shall refer to this model as the Huang-Rhys model.

Regardless of the form of the potentials $U_1(x)$ and $U_2(x)$, at sufficiently high temperatures the leading exponential in the capture cross section will have activational character $\sigma \propto \exp(-\varepsilon_2/kT)$ with an activation energy ε_2 equal to the vibrational energy in the potential $U_2(x)$ at the point of contact of the terms. At low temperatures the transition is governed by tunneling.[4,5] We show below that the temperature region corresponding to a purely activational transition is usually inaccessible in practice for deep centers. In the actual temperature region the nature of the transition is one of thermally activated tunneling. With increasing vibrational energy the probability of the thermal excitation falls off exponentially, while the tunneling probability increases exponentially. The characteristic energy E_0 at which the transition occurs (the saddle-point energy) is determined by the competition of these two processes and depends on the temperature. We show in this paper that in practice the energy E_0 is always lower than the energy ε_2. This lets on calculate the tunneling probability by a quasiclassical,[6,7] with the aid of which a result can be obtained for any form of the potentials $U_1(x)$ and $U_2(x)$.

In this paper (in a model described below) we obtain an expression for the power of the tunneling exponential as a function of the vibrational energy. By averaging the tunneling transition probability over the equilibrium distribution of the vibrations we find the temperature dependence of the saddle-point enrgy E_0 and the power Φ of the leading exponential in the capture cross section: $\sigma \propto \exp(-\Phi)$. The effective activation energy, given by the expression $kT^2(d\Phi/dT)$, turns out to be substantially small than the energy ε_2. The temperature dependence of the exponent Φ and of the activation energy is shown in Figs. 2 and 3.

The dependence of the capture cross section on the binding energy ε_T of an electron at the center is often discussed in the literature (the "energy-gap law"; see, e.g., Ref.

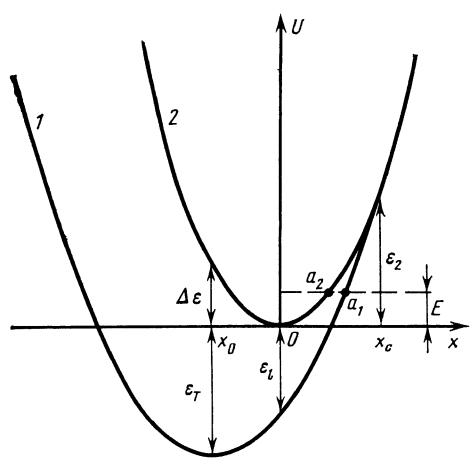

FIG. 1. General scheme of the adiabatic terms: 1) $U_1(x)$, 2) $U_2(x)$; x_c is the point of contact of the terms, x_0 is the displacement of the equilibrium position, ε_T is the thermal ionization energy, ε_l is the energy of the luminescence quantum, $\varepsilon_{\rm opt} = \varepsilon_T + \Delta\varepsilon$ is the optical ionization energy, E is the energy for which the probability of the tunneling transition is calculated, and a_1 and a_2 are the turning points.

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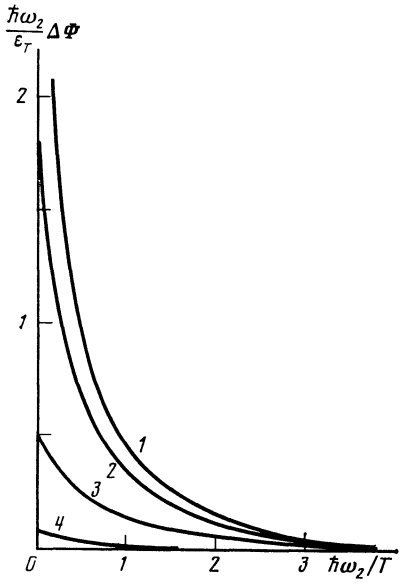

FIG. 2. Dependence of the power Φ of the exponential in the capture cross section versus the inverse temperature for various values of the parameter β: 1) 0, 2) 0.1, 3) 0.5, 4) 0.9; $\Delta\Phi = \Phi_0 - \Phi$, where Φ_0 is the value of Φ at $T = 0$ K.

8). It should be emphasized that the transition probability is not directly related to ε_T but is determined by the behavior of the potential curves in the region above the saddle-point energy E_0. A direct connection between the transition probability and ε_T arises only when some concrete model used, and the actual relation will depend on the choice of model.

We consider a model in which it is assumed that the electron binding energy is given by $\varepsilon(x) \propto (x - x_c)^2$ over a wide interval of x values including both the point of contact of the terms (x_c) are both equilibrium positions (the minima of the potential curves). This means that the "zero-radius potential" model is used at all values of the nuclear coordinate right up to the equilibrium value. Such an approximation is justified if the depth of the impurity potential well for an electron at the center is large compared to the

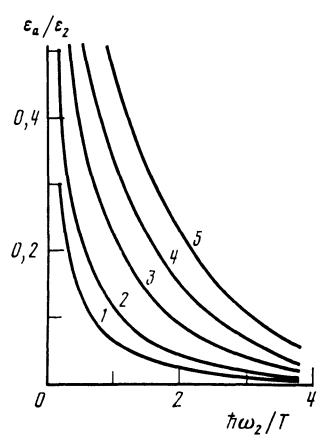

FIG. 3. Effective activation energy ε_a as a function of the inverse temperature at various values of β: 1) 0.05; 2) 0.10, 3) 0.25, 4) 0.50, 5) 0.99.

energy ε_T. The potential energy of deformation is assumed to depend harmonically on x. Then the terms are parabolas with different equilibrium positions and different vibrational frequencies.

If the level and the band edge have different symmetry types, the distortion of the terms due to their touching can occur only in a small neighborhood of the contact point. Then, for a weak electron-phonon coupling the usual (Huang-Rhys) model of two displaced parabolas with the same vibrational frequencies becomes justified. We have mad a comparison of these two models. It turns out that the temperature dependence of the capture cross section in the case of weak coupling is the same for the two models, but the value of the cross section is different. This is because the temperature dependence of the cross section is determined by the behavior of the terms in the region of the saddle-point energy, where the potential curves for the two models practically coincide, describing identical parabolas displaced vertically by ε_T. The value of the cross section, on the other hand, is determined by the behavior of the terms over the entire region above the saddle-point energy up to the point of contact of the terms. We note that for weak coupling the point of contact of the terms lies in the region of very high vibrational energies, where the behavior of the terms can be distorted by anharmonicity, and neither model is reliable for determining the magnitude of the capture cross section.

1. EXPONENTIAL DEPENDENCE OF THE MULTIPHONON TRANSITION PROBABILITY

The problem of multiphonon capture separates into two parts: calculation of the transition probability $P(E)$ at a fixed system energy E, and the averaging of this quantity over the energy distribution of the vibrations. Let us begin with the first part of the problem.

To calculate the transition probability we must determine the perturbation that causes the transition. This perturbation could be either the nonadiabiticty operator (if the transition is caused by the same local vibrations that form the terms) or the interaction of the electron with other local or lattice vibrations (with the so-called activating mode[9]). In addition, we need to know the adiabatic electronic wave functions of the initial and final states. However, both the choice of perturbation and the form of the electronic wave function will affect only the pre-exponential factor in the expression for the transition probability. The leading exponential is determined by the overlap of the vibrational wave functions corresponding to the two terms between which the transition occurs. If the transition probability is written in the form

$$P(E) = B\exp(-2s), \tag{1}$$

the argument of the exponential can be determined by the Landau method,[6] with the result[7,10] that s is given as the difference

$$s = s_2 - s_1; \quad s_i = \frac{(2M)^{1/2}}{\hbar}\int_{a_i}^{x_c} [U_i(x) - E]^{1/2}\,dx; \quad i = 1, 2, \tag{2}$$

where M is the mass of the nucleus, s_1 and s_2 are the argu-

ments of the tunneling exponentials corresponding to the tunneling of the nucleus in the potentials $U_1(x)$ and $U_2(x)$ from the turning points a_1 and a_2 to the point of contact (x_c) of the terms.[1)] It follows from expression (2) that s is determined solely by the behavior of the potential $U_1(x)$ above the minimum of the term $U_2(x)$. The behavior of $U_1(x)$ below this minimum and, in particular, the value of the ionization energy ε_T do not directly influence the value of the tunneling exponential.

Let us consider in more detail the behavior of $U_1(x)$ and $U_2(x)$. The potential $U_2(x)$, which corresponds to the absence of an electron in the center, can be assumed harmonic

$$U_2(x)={}^1/_2M\omega_2{}^2x^2. \tag{3}$$

The potential $U_1(x)$ differs from $U_2(x)$ by the electron binding energy $\varepsilon(x)$: $U(x) = U_2(x) - \varepsilon(x)$. This energy should be determined from the Schrödinger equation for the electronic wave function $\Psi(\mathbf{r})$ at a fixed value of the nuclear coordinate x. If we assume, as is customary, that the interaction energy with the local vibration is proportional to x, the Schrödinger equation will be of the form

$$H_0\psi+xV(\mathbf{r})\psi=-\varepsilon(x)\psi, \tag{4}$$

where $V(\mathbf{r})$ is some function of the electronic coordinates. The value of $V(\mathbf{r})$ is of the order of an atomic quantity. However, one often considers the case of weak coupling, when $V(\mathbf{r})$ is anomalously small. In this case the energy $\varepsilon(x)$ can be found (for sufficiently small x) by perturbation theory:

$$\varepsilon(x)=\varepsilon_0-xV_{00}, \tag{5}$$

where ε_0 is the binding energy in the absence of the electronic-vibrational interaction, V_{00} is the matrix element of the operator $V(\mathbf{r})$ on the unperturbed wave function. Then

$$U_1(x)={}^1/_2M\omega_2{}^2(x+x_0)^2-\varepsilon_T, \tag{6}$$

where $-x_0$ and ε_T are the equilibrium position of the oscillator and the thermal ionization energy of the center with allowance for the electronic-vibrational coupling:

$$\begin{gathered} x_0=V_{00}/M\omega_2{}^2; \quad \varepsilon_T=\varepsilon_0+\Delta\varepsilon; \\ \Delta\varepsilon=V_{00}{}^2/2M\omega_2{}^2=M\omega_2{}^2x_0{}^2/2. \end{gathered} \tag{7}$$

Obviously formulas (7) are valid if $x_0V_{00}\ll\varepsilon_0$, i.e., if $\Delta\varepsilon$ is small compared to ε_0 ($\Delta\varepsilon$ is the difference between the optical and thermal energies; see Fig. 1). However even in this case formula (5) and thus formula (6) are manifestly invalid in the region of the contact point x_c of the terms, where $\varepsilon(x)$ goes to zero.

Near the contact point, as we have said, it follows from general considerations that $\varepsilon(x) \propto (x - x_c)^2$. We find

$$\varepsilon(x)={}^1/_2M\omega_2{}^2\beta(x-x_c)^2, \tag{8}$$

where β is a dimensionless constant. Then near the contact point we can write the potential $U_1(x)$ in a form analogous to (6),

$$U_1(x)={}^1/_2M\omega_2{}^2[x^2-\beta(x-x_c)^2]={}^1/_2M\omega_1{}^2(x+\tilde{x}_0)^2-\tilde{\varepsilon}_T, \tag{9}$$

by the formal introduction of the variables

$$\begin{gathered} \omega_1{}^2=(1-\beta)\omega_2{}^2, \quad \tilde{x}_0=\beta(1-\beta)^{-1}x_c, \\ \tilde{\varepsilon}_T=\frac{M\omega_2{}^2\beta}{2(1-\beta)}x_c{}^2=\frac{\beta}{1-\beta}\varepsilon_2, \quad \varepsilon_2=U_2(x_c). \end{gathered} \tag{10}$$

A model exists in which formula (9) gives the behavior of the terms over the entire region from the displaced equilibrium position $-x_0$ to the point of contact of the terms. This is the case in which the binding energy of the electron is much smaller than the depth of the potential well over the entire region indicated. Then the "zero-radius" or "point" potential model is valid, and ε is proportional to $(x - x_c)^2$ over the entire range of x.[2] In this model $\tilde{\varepsilon}_T = \varepsilon_T, \tilde{x}_0 = x_0$. If we introduce a constant β as before [by formula (8)], then formulas (10) relate β to the actual physical quantities. In particular, the difference between the thermal and optical ionization energies is related to β by $\Delta\varepsilon = \beta(1-\beta)^{-1}\varepsilon_T$. If the electron–phonon interaction is taken in the form $xV(r)$, then β is related to the matrix element V_{00} appearing in (5) and (7) by the relation $\beta = V_{00}^2/2M\omega_2^2\varepsilon_0$. We note that this model has meaning only for $\beta < 1$, since for $\beta \geqslant 1$ it does not give a stable equilibrium position for a nucleus with a bound electron [for $\beta > 1$ the potential $U_1(x)$ is an inverted parabola]. However, in the region which is important for the tunneling transition potential (9) can have meaning even for $\beta \geqslant 1$, i.e., for $\omega_1^2 \leqslant 0$, but such a behavior cannot, of course, extend as far as the equilibrium position.

Calculating s_2 and s_1 by formulas (2) with potentials (3) and (9), we get

$$\begin{gathered} s_2=\frac{\varepsilon_2}{\hbar\omega_2}f(z_2), \quad f(z)=z^{1/2}+(1-z)\ln\frac{(1-z)^{1/2}}{1+z^{1/2}}, \\ z_2=\frac{\varepsilon_2-E}{\varepsilon_2}, \\ s_1=\frac{\varepsilon_2}{\hbar\omega_2}(1-\beta)^{-3/2}f(z_1), \quad z_1=\frac{\varepsilon_2-E}{\varepsilon_2}(1-\beta), \quad \beta\leqslant1, \\ s_1=-\frac{\varepsilon_2}{\hbar\omega_2}(\beta-1)^{-3/2}\{y_1{}^{1/2}+(1+y_1)\operatorname{arctg}y_1{}^{1/2}\}, \\ y_1=\frac{\varepsilon_2-E}{\varepsilon_2}(\beta-1), \quad \beta\geqslant1. \end{gathered} \tag{11}$$

Energy ε_2 is the activation energy for a transition from term 2 to term 1 (see Fig. 1). It is related to $\tilde{\varepsilon}_T$ by the expression $\varepsilon_2 = (1-\beta)\beta^{-1}\tilde{\varepsilon}_T$. For $\beta \geqslant 1$ the energy $\tilde{\varepsilon}_T$ is negative.

For tunneling from the bottom of term $U_2(x)$ (for $E = 0$) we have

$$\begin{gathered} 2s=\frac{\varepsilon_2}{\hbar\omega_2}\alpha, \quad \alpha=\frac{2\beta}{(1-\beta)^{3/2}}\left[\ln\frac{1+(1-\beta)^{1/2}}{\beta^{1/2}}-(1-\beta)^{1/2}\right]; \\ \beta\leqslant1, \\ \alpha=\frac{2\beta}{(\beta-1)^{3/2}}[(\beta-1)^{1/2}-\operatorname{arctg}(\beta-1)^{1/2}]; \quad \beta\geqslant1. \end{gathered} \tag{12}$$

Formulas (12) express the power of the tunneling exponential describing the transition from term 2 to term 1 at zero temperature in terms of the activation energy for this transition. The coefficient α varies from 0 (for $\beta\to0$) to 2 (for

$\beta \to \infty$) and is equal to 2/3 at $\beta = 1$.

Let us rewrite formula (12) for $\beta \leqslant 1$ in another form, expressing s in terms of $\tilde{\varepsilon}_T$, which has the meaning of the thermal ionization energy of the zero-radius potential model (hereafter, since we always have this model in mind, we have dropped the tilde over ε_T):

$$2s = \frac{\varepsilon_T}{\hbar\omega_2}\alpha_1; \quad \alpha_1 = \frac{2}{(1-\beta)^{1/2}}\ln\frac{1+(1-\beta)^{1/2}}{\beta^{1/2}} - 2; \quad \beta \leqslant 1. \tag{13}$$

As a rule, energies ε_2 and ε_T are large, and the case of practical interest is $E \ll \varepsilon_T, \varepsilon_2$. In this case formulas (11) give for the power of the tunneling exponential

$$2s = \frac{\varepsilon_T}{\hbar\omega_2}\alpha_1 + \frac{E}{\hbar\omega_2}\ln\frac{E}{\varepsilon_T}\eta; \quad \eta = \frac{1-\nu^2}{4e\nu^2}\left(\frac{1+\nu}{1-\nu}\right)^{1/\nu};$$
$$\nu = (1-\beta)^{1/2}. \tag{14}$$

If the constant β is small, then $\varepsilon_2 \gg \varepsilon_T$, and it makes sense to generalize formula (14) to the case of an arbitrary relationship between E and ε_T (but for $E \ll \varepsilon_2$). For this case formulas (11) give

$$2s = \frac{\varepsilon_T}{\hbar\omega_2}\ln\frac{4}{\beta e^2} - \frac{\varepsilon_T}{\hbar\omega_2}\ln\frac{\varepsilon_T+E}{\varepsilon_T} - \frac{E}{\hbar\omega_2}\ln\frac{\varepsilon_T+E}{E}. \tag{15}$$

Let us compare these formulas with those given by Huang-Rhys model. A calculation of the exponent $2s$ with a potential $U_1(x)$ corresponding to (6) will, of course, yield[7] the Huang-Rhys result for the power of the exponential (asymptotically for $\varepsilon_T \gg \hbar\omega_2$). For $E = 0$ this result (given, e.g., in Ref. 8) is of the form

$$2s = \frac{\varepsilon_T}{\hbar\omega_2}\left[2\ln\frac{1+(1-\beta')^{1/2}}{\beta'^{1/2}} - 2\frac{(1-\beta')^{1/2}}{1+(1-\beta')^{1/2}}\right];$$
$$\varepsilon_T = \frac{\beta'}{1-\beta'}\varepsilon_2. \tag{16}$$

The constant β' is introduced in such a way that the relation between ε_T and ε_2 is expressed in terms of this constant in the same way as in the zero-radius potential model. This constant is related to the "polaron shift" $\Delta\varepsilon$ by $\beta' = 4\varepsilon_T\Delta\varepsilon/(\varepsilon_T + \Delta\varepsilon)^2$. For weak coupling $\beta' \ll 1$, and for $E \ll \varepsilon_2$ the power of the exponential for the Huang-Rhys model is given by

$$2s = \frac{\varepsilon_T}{\hbar\omega_2}\ln\frac{4}{e\beta'} - \frac{\varepsilon_T}{\hbar\omega_2}\ln\frac{\varepsilon_T+E}{\varepsilon_T} - \frac{E}{\hbar\omega_2}\ln\frac{\varepsilon_T+E}{E}. \tag{17}$$

Comparing (17) and (15), we see that the Huang-Rhys model and the zero-radius potential model lead to the same energy dependence of the exponent $2s$. However, there is a difference in the constant term (the factor in the logarithm in the first term), which leads to a difference in the value of the transition probability. We note that result (17) can be obtained, under certain assumptions, by perturbation theory (see Appendix 1).

2. CALCULATION OF THE CAPTURE CROSS SECTION

The capture cross section under equilibrium conditions is determined by the probability for a transition from term U_1 to term U_2 on the average over the equilibrium distribution of the vibrations in term U_2:

$$\langle P\rangle = \sum_n f(E_n)P(E_n); \quad f(E_n) = 2\,\mathrm{sh}\frac{\hbar\omega_2}{2kT}\exp\left(\frac{-E_n}{kT}\right),$$
$$E_n = (n+{}^1/_2)\hbar\omega_2; \quad P(E_n) = B\exp[-2s(E_n)]. \tag{18}$$

In the sum for $\langle P\rangle$ the leading contribution is from the terms which have the minimum value of the exponent

$$\Phi(E) = \frac{E}{kT} + 2s(E); \quad s(E) = s_2(E) - s_1(E). \tag{19}$$

We define the saddle-point energy E_0 by the condition

$$\left(\frac{d\Phi}{dE}\right)_{E=E_0} = \frac{1}{kT} + 2\left(\frac{ds}{dE}\right)_{E=E_0} = \frac{1}{kT}$$
$$+ \frac{1}{\hbar\omega_2}\left[\ln\frac{1-z_2^{1/2}}{1+z_2^{1/2}} - \frac{1}{(1-\beta)^{1/2}}\ln\frac{1-z_1^{1/2}}{1+z_1^{1/2}}\right]_{E=E_0} = 0, \tag{20}$$

where z_1 and z_2 are defined in (11).

At small E_0 ($E_0 \ll \varepsilon_T, \varepsilon_2$) we can use formula (14) for s to obtain the the simple expression

$$E_0 = \frac{\varepsilon_T}{e\eta}\exp\left(-\frac{\hbar\omega_2}{kT}\right). \tag{21}$$

If $E_0 \ll \hbar\omega_2$ ("low" temperatures), we need keep only the first term (with $n = 0$) in the sum of $\langle P\rangle$. On the other hand, if $E_0 \gg \hbar\omega_2$ ("high" temperatures), the sum in (18) can be replaced by an integral, since it can be shown that the adjacent terms in the sum differ only slightly from one another in the important region of energies $E_n \sim E_0$. We see from (32) that $E_0 \gg \hbar\omega_2$ when

$$kT \gg \hbar\omega_2/\ln(\varepsilon_T/e\eta\hbar\omega_2).$$

Since it is assumed that $\varepsilon_T \gg \hbar\omega_2$, the "high-temperature" region begins even for $kT < \hbar\omega_2$. Then $\langle P\rangle$ and thus the capture cross section σ are proportional to $\exp(-\Phi)$, where Φ denotes the value of $\Phi(E)$ at the saddle-point energy $E = E_0$. Figure 2 shows Φ as a function of the inverse temperature for various values of the parameter β. The curves were calculated using formulas (19) and (11) with E equal to the saddle-point energy E_0 found by solving transcendental equation (20).

At small values of β the saddle-point energy, while larger than ε_T, can still remain much smaller than ε_2. Under these conditions ($\beta \ll 1$, $E_0 \ll \varepsilon_2$) we can obtain an explicit expression for E_0 using formula (15):

$$E_0 = \varepsilon_T[\exp(\hbar\omega_2/kT) - 1]^{-1}. \tag{22}$$

Then, according to (19) and (15), the power of the exponential in the capture cross section is of the form

$$\Phi = \frac{\varepsilon_T}{\hbar\omega_2}\alpha_1 + \frac{\varepsilon_T}{\hbar\omega_2}\ln\left[1 - \exp\left(-\frac{\hbar\omega_2}{kT}\right)\right]; \quad \beta \ll 1. \tag{23}$$

The values of Φ calculated with this formula are plotted as a function of the inverse temperature in Fig. 2 (curve 1).

If the temperature increases so much that E_0 becomes comparable to the activation energy, the temperature dependence of the capture cross section becomes activational; $\sigma \propto \exp(-\omega_2/kT)$. For $\beta \ll 1$, formula (22) implies that E_0

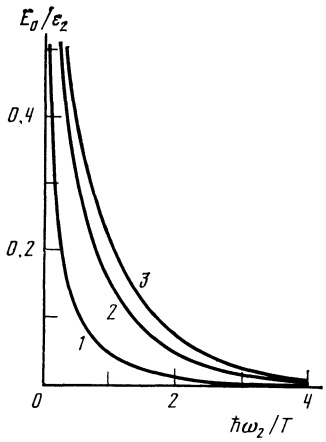

FIG. 4. Saddle-point energy E_0 versus the inverse temperature for various values of β: 1) 0.1, 2) 0.4, 3) 0.9.

approaches ε_2 for $kT > \hbar\omega_2/\beta$. Such temperatures are apparently unattainable in practice. Figure 4 shows a plot fo E_0/ε_2 from (20) as a function the inverse temperature for various values of β.

One can introduce an effective activation energy $\varepsilon_a = kT^2(d\Phi/dT)$, which characterizes the slope of the curve of $\ln\sigma$ versus $1/T$, without taking into account the temperature dependence of the pre-exponential factor. A plot of $\varepsilon_a(T)$ is shown in Fig. 3. It is seen that ε_a remains smaller than ε_2 at all temperature of interest, and the activational behavior is not attained.

The capture cross section can be written in the form

$$\sigma = Ae^{-\Phi}. \tag{24}$$

To evaluate the pre-exponential factor A we need to choose a concrete form of the perturbation causing the transition and a specific dependence of the electronic wave function ψ on the nuclear coordinate x. Let us take the perturbation to be the nonadiabaticity operator. Adiabatic perturbation theory generally does not give the exact result (see, e.g., Ref. 11), but it does give the correct power of the exponential and usually the correct order of magnitude of the pre-exponential factor. For our problem we can verify this directly in the limiting cases (see Appendix 2).

The dependence of ψ on x has been discussed in many papers. A summary of these discussions is given by Huang.[12] The earlier papers used the electronic wave functions obtained in the first order of a perturbation theory in the electron-phonon interaction from Eq. (4). Lax[13] called this the Condon approximation. Kovarskiĭ and co-workers first pointed out that this approximation leads to an underestimate of the transition probability and proposed another (the so-called non-Condon) approximation. In a somewhat modified form due to Ridley,[14] this approximation consists of the inclusion of the diagonal (in the electron states) part of the electron-phonon interaction in the electronic Hamiltonian. The electronic wave functions are found in the first order of a perturbation theory in the remaining off-diagonal part. Huang[12] showed that the non-Condon approximation is completely equivalent to the so-called static-coupling model.[15,16] He also showed that this approximation gives the correct answer to first order in the off-diagonal part of the electron-phonon interaction.

For obtaining the correct pre-exponential factor, however, this approximation is insufficient (see Appendix 1). The transition matrix element contains an integral of a highly oscillatory function of the nuclear coordinate x. In this case what is most important is the behavior of the integrand in the complex x plane in the neighborhood of the point of contact of the terms,[6] where the binding energy of the electron goes to zero. Perturbation theory in the electron-phonon interaction cannot be used to describe the behavior of the electronic wave function near this point. Here, however, the zero-radius potential approximation, which describes a shallow level in a deep potential well and the continuum states in the presence of this level, applies very well. The suitability of the zero-radius potential model for treating nonadiabatic transitions froma discrete level to the continuum was first pointed out by Demkov and Devdariani[17] in connection with the problem of the detachment of an electron from a negative ion during collisions. This approximation was actually used by Morgan[18] in the problem of multiphonon capture, but in that study the transition matrix element was determined only by computer calculations.

Using the zero-radius potential model, we get the following expression for the pre-exponential factor (see Appendix 2):

$$A = A_0 \frac{16\sqrt{2}}{27\beta}\left(\frac{\hbar\omega_2}{kT}\right)^2 \times \operatorname{sh}\left(\frac{\hbar\omega_2}{2kT}\right)\frac{(1-z_0)^{1/2}[1-(1-\beta)z_0]^{1/2}}{\{z_0^{1/2}\ln[(1+z_0^{1/2})/(1-z_0^{1/2})]\}^{3/2}}; \tag{25}$$

$$z_0 = 1-\frac{E_0}{\varepsilon_2}, \quad \varepsilon_2 = (1-\beta)\varepsilon_T\beta^{-1}, \quad A_0 = \frac{g\omega_2}{N_c\langle v\rangle}\left(\frac{kT}{\hbar\omega_2}\right)^2,$$

where E_0 is the saddle-point energy, N_c is the effective density of states in the band from which the capture occurs, $\langle v\rangle$ is the average thermal velocity of a free charge carrier, and g is the degeneracy of the level. Using the standard expression for N_c and for $\langle v\rangle$, we obtain the following formula for A_0:

$$A_0 = \frac{\pi^2 g}{2n}\frac{\hbar}{m\omega_2}, \tag{26}$$

where n is the number of valleys in the band and m is the effective mass of a charge carrier. For $\beta \ll 1$ the expression for A can be written in explicit form with the aid of (22):

$$A = A_0\frac{8\sqrt{2}}{27}\left(\frac{\hbar\omega_2}{kT}\right)^2\left\{\ln\left[\frac{4}{\beta}(e^{\hbar\omega_2/kT}-1)\right]\right\}^{-3/2}. \tag{27}$$

3. COMPARISON WITH EXPERIMENT

The formulas for the capture cross section [(24)–(26), (11), (19), (20)] contain three parameters of the center: ε_T, ω_2, and β. The thermal ionization energy ε_T can be determined from Hall measurements or by capacitive spectroscopy. The constant β characterizes the difference in the frequencies of the local vibrations in the absence and in the

presence of an electron at the center: $\omega_2^2 - \omega_1^2 = \beta\omega_2^2$. From the photoionization data one can determine the optical ionization energy $\varepsilon_{\rm opt}$, and from impurity-band luminescence measurements one can determine the luminescence quantum ε_l. It is easy to see that the constant β is expressed in terms of these data through the formula

$$\beta=(\varepsilon_{opt}+\varepsilon_l-2\varepsilon_T)/(\varepsilon_{opt}-\varepsilon_T). \tag{28}$$

This relation is valid regardless of whether the terms touch or intersect. If they touch, then there should be one more relation among the parameters:

$$\Delta\varepsilon/\varepsilon_T=(\varepsilon_{opt}-\varepsilon_T)/\varepsilon_T=\beta/(1-\beta). \tag{29}$$

Comparing (28) and (29), we get the relation

$$\varepsilon_{opt}\varepsilon_l=\varepsilon_T^2, \tag{30}$$

which can be regarded as an applicability criterion for the zero-radius potential model. Actually relation (30) is informative when $\varepsilon_{\rm opt}$ and ε_l are not too different from ε_T. In the Huang-Rhys model, in which the frequencies are the same, a different condition from (30) should hold: $\varepsilon_{\rm opt} + \varepsilon_l = 2\varepsilon_T$. If $\varepsilon_{\rm opt}$ and ε_l are close to ε_T, this condition means that the electron-phonon coupling is weak. In this case the two models are indistinguishable.

Let us consider as an example the 2 state of oxygen in GaP; this state has been studied in detail by Henry and Lang.[1] The values obtained for the thermal and optical ionization energies of an electron from this level to the conduction band are $\varepsilon_T = (0.89 \pm 0.06)$ eV, $\varepsilon_{\rm opt} \approx 1.95$ eV. Instead of ε_l, Henry and Lang give the values of the optical ionization energy $\varepsilon_{\rm opt}^p$ for the ejection of a hole from the center into the valence band. According to Ref. 1, $\varepsilon_l = E_g - \varepsilon_{\rm opt}^p$. The data of Ref. 1 yields $\varepsilon_l = 0.41$ eV (all the energies are taken at 400 K). Then we obtain identical values for ε_T and $(\varepsilon_{\rm opt}\varepsilon_l)^{1/2}$, close to 0.9 eV. The coincidence of these values argues in favor of our adopted model. From (28) and (29) we find $\beta = 0.55$. The terms constructed from these data in Ref. 1 actually do touch each other and correspond to different vibrational frequencies $\omega_2^2 - \omega_1^2 \approx 0.56\omega_2^2$ However, the shape of the terms (Fig. 13 of Ref. 1) implies that $\omega_2 = 0.7$ eV (the formula $\varepsilon_2 = (1-\beta)\varepsilon_T\beta^{-1}$ implies that $\varepsilon_2 = 0.73$ eV.) This result is in sharp disagreement with the data on the capture cross section if it is assumed that the multiphonon transition has an activational character. However, if it is taken into account that the nature of the transition is one of thermally activated tunneling, then the scheme of terms constructed in Ref. 1 can be made consistent with the data[1] on the capture cross section. Figure 5 shows the theoretical curve of $\sigma = A\exp(-\Phi)$ as a function of inverse temperature, together with the experimental points from Ref. 1. In the calculation we took, in accordance with the experiment,[1] $\varepsilon_T = 0.89$ eV, $\beta = 0.55$. The energy of the vibrational quantum $\hbar\omega_2$ and the pre-exponential factor A_0 were adjustable parameters. The values adopted were $\hbar\omega_2 = 280$ K and $A_0 = 1.4 \approx 10^{-13}$ cm^2. A calculation using formula (26) gives $A_0 = 2.5 \approx 10^{-13}$ for $g = 2$, $n = 3$, and $m = 0.36$ (the density-of-states mass).

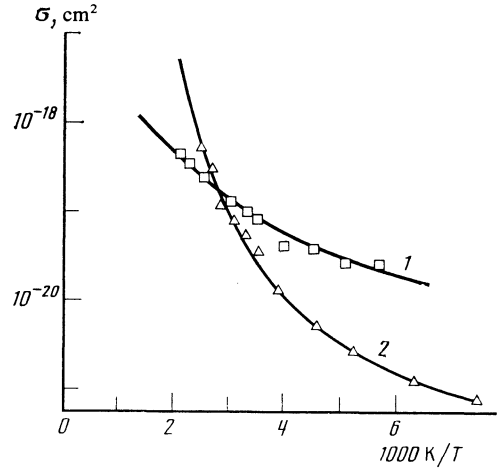

FIG. 5. Approximation of the experimental data on the capture cross section by the formula $\sigma = A\exp(-\Phi)$: □) oxygen, state 2 in GaP,[1] △) B level in GaAs.[19] The curves are calculated for: 1) $\varepsilon_T = 0.89$ eV, $\beta = 0.55$, $\hbar\omega_2 = 280$ K, $A_0 = 1.4\cdot10^{-13}$ cm^2; 2) $\varepsilon_T = 0.8$ eV, $\beta < 1$, $\hbar\omega_2 = 500$ K, $A\exp(-\Phi_0) \approx 10^{-21}$ cm^2.

Thus, both the temperature dependence and the value of the capture cross section can in fact be made consistent with the theory by means of a single adjustable parameter—the frequency of the local vibrations.

There are also data on the capture of electrons over a wide temperature range for the so-called B level in GaAs (a natural defect).[1,19] Measurements of the thermal and optical ionization energies[19] indicate that β is small for this center ($\beta \approx 0.1$). Figure 5 shows the calculated curve of $\sigma = A\exp(-\Phi)$ corresponding to the limit of small β (the values of Φ correspond to curve 1 in Fig. 2), together with the experimental points from Ref. 19. Agreement is reached for $A\exp(-\Phi_0) \approx 10^{-21}$ cm^2, where Φ_0 is the value of Φ at $T = 0$ K, $\hbar\omega_2 = 500$ K, $\varepsilon_T = 0.8$ eV. The measured value[1,19] is $\varepsilon_T = 0.79$ eV. Estimates of $A\exp(-\Phi_0)$ made with the aid of formulas (27) and (23) are extremely sensitive to the value of β. A value $\sim 10^{-21}$ cm^2 is obtained for $\beta \approx 0.2$–0.3. As we mentioned back in the Introduction, estimates of the cross section for small β are unreliable.

In conclusion we note that both the value of the multiphonon capture cross section and its temperature dependence are extremely sensitive to the parameters of the center. Therefore, estimating the cross section with the aid of the theoretical formulas by proceeding from plausible approximate values of the parameters may not give even the correct order of magnitude (for example, changing the frequency of the local vibrations by 10% can change the estimates by several orders of magnitude). On the other hand, the measured values of the capture cross section can be used to recover the parameters of the center and to check their reasonableness and agreement with the data of other experiments.

We are grateful to M. K. Sheĭnkman, who in large measure stimulated this study.

APPENDIX 1

Perturbation-theory derivation of formula (17)

We obtain formula (17) by using perturbation theory to consider a process in which $N = \varepsilon_T/\hbar\omega_2$ phonons are

created and the electron goes from state 1 to state 0. We introduce a dimensionless coupling constant G by proceeding from the relation $V_{00}x = G\hbar\omega_2(b^+ + b)$, where b^+ and b are the phonon creation and annihilation operators. Since $x = (b^+ + b)(\hbar/2M\omega_2)^{1/2}$, we have

$$G=(V_{00}/\hbar\omega_2)(\hbar/2M\omega_2)^{1/2}. \tag{1.1}$$

We take into account only that term of the perturbation series for which there is an electron there is an electron bound to the center in all the intermediate states and for which very virtual transition is accompanied by the emission of a phonon. Then the matrix element of the Nth order perturbation series will contain a factor $(G\hbar\omega_2)^N$ and $(N-1)$ energy denominators of the form $\varepsilon_0 - \hbar\omega_2$, $\varepsilon_0 - 2\hbar\omega_2, \ldots, \varepsilon_0 - (N-1)\hbar\omega_2$. The product of these denominators is equal to $(\hbar\omega_2)^{(N-1)}(N-1)!$. In addition, the matrix elements of the creation operator give factors of $\sqrt{1}\sqrt{2}\ldots\sqrt{N}$. The leading exponential in the expression for the probability of a transition involving the emission of N phonons will thus be governed by a factor $G^{2N}/N!$. Using Stirling's formula, we find that

$$P\sim\exp\left(-N\ln\frac{N}{G^2e}\right). \tag{1.2}$$

Substituting into this expression the value of G from (1.1) and using (7), we find that $P\approx\exp(-2s)$, where s is determined exactly by formula (17) for $E=0$.

Let us now consider an N-phonon emission process under the condition that there are $N_1 = E/\hbar\omega_2$ phonons in the initial state. Then the factor originating from the matrix elements of the creation operators will be $\sqrt{N_1+1}\sqrt{N_1+2}\ldots\sqrt{N_1+N}$ and, consequently, the probability of this process will differ from the probability for $E=0$ by a factor of $(N+N_1)!/N!N_1!$. We then obtain formula (17) for the power of the exponential of the transition probability.

Let us now consider the terms we have dropped from the perturbation series. Among these is a term which, for example, contains a factor $V_{01}V_{10}/2\hbar\omega_2$ instead of $V_{00}^2/(\varepsilon_0 - 2\hbar\omega_2)$. It is clear that this term cannot be dropped if $\varepsilon_0 \ll \hbar\omega_2$. Hence we see that it is incorrect to keep only the first term of the expansion in the off-diagonal elements of the electron-phonon interaction (as is done in the non-Condon approximation), at least for determining the pre-exponential factor.

APPENDIX 2

Calculation of the pre-exponential factor in the capture cross section

It is convenient to first calculate the thermal-ionization probability $\langle W\rangle$ and then fo find the capture cross section by using the principle of detailed balance:

$$\sigma=\frac{g\langle W\rangle}{N_c\langle v\rangle}\exp\left(\frac{\varepsilon_T}{kT}\right)\sinh\left(\frac{\hbar\omega_2}{2kT}\right)\Big/\sinh\left(\frac{\hbar\omega_1}{kT}\right), \tag{2.1}$$

where g is the degeneracy of the level, N_c is the effective density of states in the band, and $\langle v\rangle$ is the average velocity of the electron. Let us calculate the matrix element of the nonadiabaticity operator between states 1 (a bound electron and the nucleus) and K (a free electron with wave vector K and the nucleus):

$$V_{1K}=-\frac{\hbar^2}{M}\int dx\,\varphi_1^*(x)\frac{\partial\varphi_K(x)}{\partial x}M_K,\quad M_K=\int d^3r\,\psi_1^*\frac{\partial\psi_K}{\partial x}. \tag{2.2}$$

Here M_K is the electronic matrix element, ψ_1 and ψ_2 are the electronic wave vectors, which depend on x as on a parameter. The second-derivative term in the nonadiabaticity operator has been dropped [it is smaller than other terms by a factor of $(m/M)^{1/2}$]. The wave functions φ_1 and φ_K are quasiclassical functions describing the motion of the nucleus (with the same energy E) in the potentials $U_1(x) = U_2(x) - \varepsilon(x)$ and $U_K(x) = U_2(x) + \varepsilon_K$, where $\varepsilon(x)$ and $\varepsilon_K = \hbar^2K^2/2m$ are the binding energy of an electron at the center and the energy of a free electron in the band, respectively, and $U_2(x)$ is the potential energy of the nucleus in the absence of an electron. The integration in the first of formulas (2.2) can be done from $-\infty$ to a point x_1 lying between the turning point a_1 and the point of contact of the terms, x_c, since the discarded part of the integral is proportional to the product of the tunneling exponentials, whereas the integral itself is proportional to their ratio (see below). The answer does not depend on the choice of the point x_1 in the indicated interval. The integral V_{1K} can be evaluated by the Landau method (Sec. 51 of Ref. 6), whereby the function φ_1 is broken into two parts: $\varphi_1 = \varphi_1^+ + \varphi_1^-$ (respectively $V_{1K} = V_{1K}^+ + V_{1K}^-$) and the integration contour for V_{1K}^+ is displaced into the upper half-plane of the complex variable x. The saddle point x_K is determined by the condition $U_1(x) = U_K(x)$, i.e., $\varepsilon(x_K) = -\varepsilon_K$. This point is close to the point x_c [the point of intersection of the terms $U_1(x)$ and $U_2(x)$], which is determined by the condition $\varepsilon(x_c) = 0$.

The electronic wave functions near the point x_c are of the form

$$r\psi_1=\left(\frac{\varkappa}{2\pi}\right)^{1/2}e^{-\varkappa r};\qquad r\psi_K=\frac{1}{(2\pi R)^{1/2}}\sin(Kr+\delta);$$
$$e^{i2\delta}=\frac{\varkappa-iK}{\varkappa+iK}, \tag{2.3}$$

where $\varkappa = (2m\varepsilon(x))^{1/2}/\hbar$. R is the radius of the normalization sphere, and $\varepsilon(x)$ is given by (8). Evaluating M_K, we obtain the expression

$$M_K=\frac{\omega_2}{\hbar}\left(\frac{mM\beta}{R}\right)^{1/2}\frac{K\varkappa^{1/2}}{(\varkappa^2+K^2)^{3/2}},$$

from which we see that the electronic matrix element has an anomaly right at the saddle point. It can be shown that $\varepsilon_2 - E \gg \varepsilon_s$, where $\varepsilon_s = [4\varepsilon_2^3(\hbar\omega)^2/\beta^2]^{1/5}$, the width of the saddle is larger than x_K. Then we can take the point $x = x_c$ as the saddle and evaluate the integral V_{1K}^+ over contour C in Fig. 6. The part of the contour between x_1 and x_c falls out of the sum $V_{1K}^+ + V_{1K}^-$. As a result we obtain

$$|V_{1K}|^2=\frac{16\hbar^2\omega_1\varepsilon_K}{27\pi R(2m\beta(\varepsilon_2-E))^{1/2}}\times\exp(2s_1-2s_K), \tag{2.4}$$

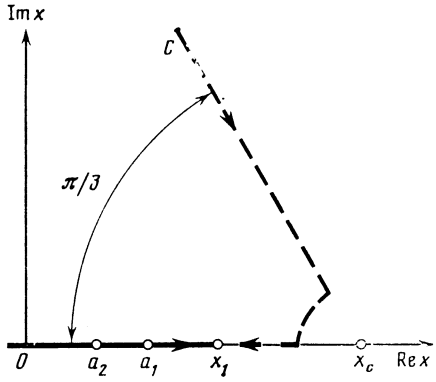

FIG. 6. Integration contour for evaluating V_{1K}^{+}. The solid line is the original contour; the dashed line is contour C.

where s_i is given by (2).

To obtain the probability of thermal ionization from the level E, the transition probability expressed by the usual perturbation-theory formula must be summed over all the final states [i.e., over all values of K in the normalization sphere and over all energy levels E_2 of the oscillator with potential $U_2(x)$]. The result is

$$W(E)=\frac{\omega_1}{2\pi}\frac{32}{27\beta^{1/2}}\sum_{E_2<E}\left(\frac{E-E_2}{\varepsilon_2-E}\right)^{1/2}\exp[2s_1-2s_2(E_2)], \quad (2.5)$$

where $s_2(E_2)$ is given by (2) with E_2 in place of E. The energy E differs from E_2 by the energy of the escaping electron. Expanding $s_2(E_2)$ in powers of $(E-E_2)$ and keeping the first two terms, we get

$$s_2(E_2)=s_2+\frac{\tau}{\hbar}(E-E_2),$$

$$2\tau=\int_{a_2}^{x_c}\left(\frac{2M}{U_2-E}\right)^{1/2}dx=\omega_2^{-1}\ln\frac{\varepsilon_2^{1/2}+(\varepsilon_2-E)^{1/2}}{\varepsilon_2^{1/2}-(\varepsilon_2-E)^{1/2}}. \quad (2.6)$$

The quantity τ can be interpreted as the tunneling time (from the turning point to the point at which the terms touch) in the potential $U_2(x)$ at energy E. The energy of the electrons escaping on thermal ionization is thus of order $\hbar/\tau$. By averging $W(E)$ over the vibrational energy in the initial state with the equilibrium distribution function

$$f_0=2\sinh(\hbar\omega_1/2kT)\exp[-(E+\varepsilon_T)/kT],$$

we obtain $\langle W\rangle$ and, using (2.1), the expression for σ given by (24) and (25) in the main text. We note that since the width of the saddle in the sum over E is greater than $\hbar\omega_2$ for $E_0>\hbar\omega_2$, the sum over E and E_2 in the calculation of $\langle W(E)\rangle$ can be replaced by an integral.

Let us also give the formula for $W(E)$ obtained from (2.5) upon the replacement of the sum by an integral, and with allowance for (2.6):

$$W(E)=\frac{\omega_1}{2\pi}\frac{16\pi^{1/2}}{27\beta^{1/2}}\left(\frac{\hbar\omega_2}{\varepsilon_2-E}\right)^{1/2}\times\left[\ln\frac{\varepsilon_2^{1/2}+(\varepsilon_2-E)^{1/2}}{\varepsilon_2^{1/2}-(\varepsilon_2-E)^{1/2}}\right]^{-3/2}\exp(-2s). \quad (2.7)$$

Usually values $E\ll\varepsilon_2$ are important, but it is interesting to note that for E close to ε_2 ($\varepsilon_2-E\ll\varepsilon_2$), formula (2.7) gives

$$W(E)=\frac{\omega_1}{2\pi}\frac{4\pi^{1/2}}{27}\frac{1}{\lambda^{5/4}}\exp\left(-\frac{8}{15}\lambda^{5/2}\right), \quad \lambda=\frac{\varepsilon_2-E}{\varepsilon_s}, \quad (2.8)$$

which, up to a factor of 16/27, agrees with the result obtained by Demkov and Devdariani[17] using a completely different method. Those authors considered the liberation of an electron during the classical motion of the nucleus in the field of a constant force F. Near the touching point, where the force $F=-dU_1/dx=-dU_2/dx$ is the same for both terms, this formulation of the problem is obviously justified. It was learned in Ref. 17 that the region of nonadiabatic behavior of the electron encompasses an interval of nuclear energies E of the order of

$$\varepsilon_s=[\hbar^2F^6/2M^3\omega_2^4\beta^2]^{1/5}$$

around the value $E=\varepsilon_2$. For $E=\varepsilon_2$ the turning point of the nucleus coincides precisely with the point x_c at which the electron binding energy $\varepsilon(x)$ goes to zero. According to Ref. 17, for $E=\varepsilon_2$ the probability that an electron will be liberated in a single transition is 0.62, for $E-\varepsilon_2\gg\varepsilon_s$ this probability tends toward unity as $1-\pi/16|\lambda|^{5/2}$, and for $\varepsilon_2-E\gg\varepsilon_s$ it is given by formula (2.8) without the factor $(16/27)(\omega_1/2\pi)$. We note that the parameter $|\lambda|^{5/2}$ has a simple physical meaning. It is the ratio of two times: the time $t_1=(2M|E-\varepsilon_2|)^{1/2}|F|$ over which the nucleus traverses the distance from the point x_c to the turning point (the tunneling time if $E<\varepsilon_2$) and the time $t_2=\hbar/\varepsilon(x)$ over which the electron traverses a distance of the order of the width of its wave function at the turning point. Of course, the adiabatic approximation is valid for $|\lambda|\gg1$.

For E close to ε_2, when the transition probability is large, one might wonder if $f(E)$ is different from the equilibrium function f_0. Such a difference could arise on account of the departure of the electrons from the bound state, leading to a depletion of the distribution near $E\approx\varepsilon_2$. In order for there to be no depletion, the processes which establish thermodynamic equilibrium in the vibrational subsystem must be sufficiently intense. The role of these processes is played by the interaction of the local vibrations with the lattice phonons. It can be shown that $f(E)$ will not differ from the equilibrium distribution if

$$\gamma(\varepsilon_2+\varepsilon_T)/kT\gg W(E),$$

where γ is the damping coefficient of the local vibrations.

[1)]Formula (2) refers to the case when the energies of the initial and final states are the same. If the transition is caused by an activating mode, this corresponds to the neglect of the energy of the corresponding phonon. Allowance for the energy of the activating phonon $\hbar\omega_p$ would mean that the expressions for s_1 and s_2 would be taken at different energies $E_1=E_2\pm\hbar\omega_p$ and the point of contact x_c of the term swould be the point at which $U_1-E_1=U_2-E_2$.

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