Multiphoton ionization of deep centers in semiconductors in an electric field

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Analytic expressions are obtained for probability of ionization by a thermal field. In weak fields, the logarithm of the probability increases linearly with the square of the field. In strong fields the probability is determined by electron tunneling from a bound state with optical binding energy. The results agree with the experimental data.

In thermal ionization of a deep impurity center, the electron receives the necessary energy from the crystal lattice. This energy is usually much higher than the characteristic energy of the phonon, so that the process should be regarded as multiphonon. It is natural to assume that for a bound electron the principal role is played by the interaction with the local vibration of the center. This can serve as a basis for a model in which the lattice (henceforth referred to as "nucleus") is described by one configurational coordinate. On the scheme of the adiabatic terms (Fig. 1), thermoionization is a transition of the system from term U_1 corresponding to the bound state of the electron on the center, to term U_2 corresponding to the ionized center. It is easiest for this transition to proceed when the nucleus vibrational energy is close to the energy corresponding to the term crossing. The latter energy, however, is high ($\varepsilon_T + \varepsilon_2$ in Fig. 1), such a (thermoactivation) process has low probability at not too high temperatures. At real temperatures, the thermoionization proceeds usually via tunneling of the nucleus from term U_1 to term U_2 at nucleus vibration energies only slightly exceeding the thermal binding energy ε_T (Ref. 1).

In an electric field it becomes possible to produce ionization accompanied by electron tunneling (Fig. 2). The final state in such a process corresponds to terms located below the term U_2 (dashed curves—terms U_ε in Fig. 1). Tunneling by the nucleus is facilitated by lowering the term U_ε, but electron tunneling, on the contrary, becomes more

difficult. The competition between these two factors determines the optimal energy of the emitted electrons, and by the same token the dependence of the ionization probability on the electric field. The higher the electric field strength, the easier for the electron to tunnel, the greater the drop of the term U_ε, and the higher the ionization probability.

The presented analysis of thermofield ionization singles out two limiting cases of weak and strong fields. Roughly speaking, the difference between weak and strong fields lies in the ratio of F to F_0, where F is the force acting on the electron in the electric field, and the characteristic field $F_0 = 2(2m\varepsilon_T)^{1/2}\omega$, where ω is the nucleus-vibration frequency and m is the electron effective mass. More accurate criteria are given below.

In weak fields, the influence of the field on the thermoionization probability is described by the relation $\ln(W/W_0) = F^2\tau^3/3\hbar m$, where τ has the meaning of the time of tunneling of the electron from the turning point to the term encounter point X_c (see Fig. 1). At $k_B T < \hbar\omega$, the temperature dependence of τ is given by $\tau = \tau_0 + \hbar/2k_B T$, where k_B is the Boltzmann constant. The quadratic dependence of the logarithm of the probability of the thermoemission from the field as well as the linear dependence of τ on the reciprocal temperature agrees well with the experimental data on the ousting of carriers from deep levels in silicon, and the slope of the linear plot of τ vs T^{-1} is close to the theoretical one (see §3 below, and also Ref. 2, where the results of the theory for a weak field are briefly described and compared with the
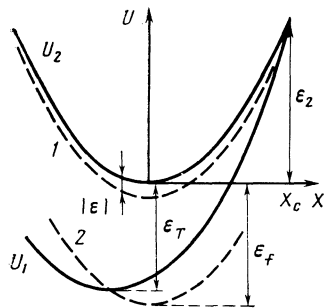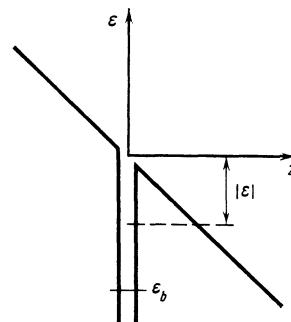

FIG. 1. Scheme of adiabatic term U of nuclear motion. X—configurational coordinate. Solid curves: U_1—electron bound to center, U_2—electron detached from center and located at the bottom of the conduction band ($\varepsilon = 0$). Dashed curves—terms U_ε in electric field: 1—characteristic term U_ε in a weak electric field, 2—in the limiting case of a strong field. ε_T—thermal binding energy. ε_f—field binding energy.

FIG. 2. Energy scheme for electron motion in an electric field directed along the z axis (ε_b—binding energy, ε—energy of emitted electron).

experimental data of Sah *et al.*[3,4]).

In strong fields the optimal location of the term U_ε is determined entirely by the most favorable conditions for the passage of the nucleus (dashed curve 2 of Fig. 1). The ionization has the character of cold emission, and its probability is determined by electron tunneling from a bound to a free state. It turns out here, however, that the most favorable conditions for the passage of the nucleus occur when the binding energy ε_f of the electron exceeds the thermal binding energy ε_T. This increase is due to the electron-phonon interaction, and ε_f coincides with the optical binding energy. The temperature correction to the argument of the tunnel exponential was also obtained.

Multiphonon thermofield emission was considered earlier in a number of papers.[5-10] The authors restricted themselves only either to the thermoactivation regime[5,7,10] (which usually sets in above room temperature), or presented their results in a form that requires laborious numerical calculations.[6,8,9] In the most extensive study, Makram-Ebeid and Lannou[9] use, following Oppenheimer, the potential energy of an electron in an external electric field as the perturbation that causes the transitions. Since the ionization probability vanishes in the absence of a field in this calculation method, they propose simply to add to the calculation result the probability of thermoemission in a zero field. This method, however, is unsubstantiated and leads to an incorrect dependence of the thermoemission probability in the weak fields in which the experimental data for silicon were mainly obtained (see §3 below).

§1. EXPONENTIAL DEPENDENCE

In the adiabatic approximation, the state of the electron is determined by the instantaneous position of the nucleus, and the nucleus itself moves in an effective potential $U(X)$, where X is the configuration coordinate of the nucleus. In Fig. 1 the term U_2 is the potential energy of the nucleus without the electron. Parallel to U_2 are the terms $U_\varepsilon = U_2 + \varepsilon$, which correspond to the electron-plus-nucleus system when the electron is detached from the center and has an energy ε. Values $\varepsilon < 0$ are possible in the presence of a field (Fig. 2).

The term $U_1 = U_2 - \varepsilon_b(X)$ is the potential energy of the nucleus when the electron is bound to the center, and $\varepsilon_b(X)$ is the binding energy. When the nucleus moves, the binding energy varies and the point $X = X_c$ corresponds to vanishing of the bound state ($\varepsilon_b(X_c) = 0$). This is the point at which the terms U_1 and U_2 cross. An adiabatic transition of the electron from the bound state into a free one with energy ε takes place at the point X_ε at which the terms U_1 and U_ε cross. If the energy level E of the nucleus lies below this crossing point, the transition is via tunneling of the nucleus from term U_1 to term U_ε. The transition probability of the nucleus contains then, according to Ref. 11, the exponential $\exp(-2|s_2 - s_1|)$, where

$$s_1 = \frac{(2M)^{1/2}}{\hbar} \int_{a_1}^{X_\varepsilon} (U_1 - E - \varepsilon)^{1/2} \, dX, \qquad s_2 = \frac{(2M)^{1/2}}{\hbar} \int_{a_2}^{X_\varepsilon} (U_2 - E)^{1/2} \, dX \tag{1}$$

are the actions accumulated by tunneling from the turning points a_1 and a_2 to the term crossing point X_ε, and M is the mass of the nucleus. The energy E is reckoned from the bottom of the parabola U_ε. The probability of the electron transition from the bound to a free state with energy $\varepsilon < 0$ also contains an exponential corresponding to electron tunneling through a triangular potential barrier (Fig. 2). As a result, the system transition probability is of the form

$$W_{1k} \infty \exp\left[-2|s_2 - s_1| - \tfrac{4}{3}(2m)^{1/2} |\varepsilon|^{3/2}/\hbar F \right],$$

where F is the force exerted on the electron by the electric field. To calculate the ionization probability this expression must be averaged over the equilibrium distribution of the nucleus in energy and integrated over the final energies ε of the electron. The result, with exponential accuracy, is $W \propto \exp(-\Phi_c)$, where Φ_c is the lowest value of the function

$$\Phi(E, \varepsilon) = \theta(E, \varepsilon) + \tfrac{4}{3}(2m)^{1/2} |\varepsilon|^{3/2}/\hbar F, \tag{2}$$

and $\theta(E,\varepsilon)$ is given by

$$\theta(E, \varepsilon) = 2|s_2 - s_1| + (E + \varepsilon_T + \varepsilon)/k_B T, \tag{3}$$

where ε_T is the thermal binding energy of the electron (see Fig. 1). Minimization of the function $\Phi(E,\varepsilon)$ with respect to the variables E and ε leads to equations for the optimal values of E_0 and ε_0:

$$2\tau_2 \mp 2\tau_1 = \hbar/k_B T, \tag{4}$$

$$2\tau_2 = 2(2m)^{1/2} |\varepsilon|^{1/2}/F, \tag{5}$$

where $\tau_i = \hbar|\partial s_i / \partial E|$ have the meaning of the tunneling times of the nucleus from the corresponding turning points to the term-crossing point. The upper sign in (4) pertains to the case when the term-crossing point X_ε is located to the right of the classical turning points, and the lower to the case when X_ε lies between a_1 and a_2.

1. We consider first the case of weak electric fields. In this case ε is small and can be neglected in Eq. (4). This equation determines then the optimal value of E_0, which does not depend on Equation (5) yields the optimal value $|\varepsilon_0| = F^2 \tau^2/2m$, and for τ we have

$$\tau = \tau_{10} + \hbar/2 k_B T, \tag{6}$$

where τ_{10} denotes the value of τ_1 at $\varepsilon = 0$ and $E = E_0$.

Expanding the function θ in powers of ε and confining ourselves to the first term of the expansion, we get

$$\theta(E_0, \varepsilon) = \theta(E_0, 0) + 2\tau\varepsilon/\hbar. \tag{7}$$

Substituting this expression in (2) and using the expression $|\varepsilon_0| = F^2 \tau^2/2m$, we get

$$\Phi_c = \theta(E_0, 0) - F^2 \tau^3/3\hbar m. \tag{8}$$

The explicit field dependence of the ionization probability in a weak electric field is thus

$$W = W_0 \exp(F^2 \tau^3/3\hbar m), \tag{9}$$

where W_0 is the thermoionization probability in a zero field.

Note that this expression was obtained without any assumption whatever concerning the form of the potential curves.

We determine now the temperature dependence of τ. At low temperatures ($k_B T < \hbar\omega$), the optimal energy level E_0 lies near the bottom of the term U_2 (Ref. 1). According to (6), τ has then a linear dependence on T^{-1}:

$$\tau = \tau_0 + \hbar/2k_B T, \tag{10}$$

where τ_0 denotes the value of τ_1 at $E = \varepsilon = 0$.

The constant τ_0 determines the variation of the term U_1, i.e., the dependence of the binding energy ε_b on the coordinate of the nucleus. Three models are used in the literature: 1) The model of Huang and Rhys,[12] in which it is assumed that this dependence is linear. We write it in the form $\varepsilon_b = \beta M \omega^2 X_c (X_c - X)/2$, where β is the coupling constant and ω the frequency of the vibrations on the term U_2. In his model the curves U_1 and U_2 are two parabolas that are moved apart and have the same vibration frequency. In fact, when the level emerges to the continuum (near the point X_c) we should have $\varepsilon_b \sim (X_c - X)^2$, i.e., the terms should touch rather than cross. Nonetheless, the model of Huang and Rhys can be a good approximation if the tangency region is small or if the symmetry of the level does not coincide with that of the edge of the band. 2) In Ref. 1 was considered a model in which the quadratic relation $\varepsilon_b = \beta M \omega^2 (X_c - X)^2/2$ is preserved in the entire range of X (the tangency model). The terms U_1 and U_2 correspond then to different vibration frequencies $\omega_1 = \omega(1-\beta)^{1/2}$. 3) The Kubo model,[13] in which the terms U_1 and U_2 have different frequencies but a common equilibrium point. They cross and the $\varepsilon_b(X)$ dependence must be written in the form $\varepsilon_b = \beta M \omega^2 (X_c^2 - X^2)/2$, and then ω_1 and $\omega(1+\beta)^{1/2}$. In these models τ_0 is of the form

$$\tau_0 = \frac{1}{2\omega} \ln C, \quad \ln C = \frac{\omega}{\omega_1} \ln \frac{[1+(\varepsilon_T/\varepsilon_2)]^{1/2}+1}{[1+(\varepsilon_T/\varepsilon_2)]^{1/2}-1}, \tag{11}$$

with $\varepsilon_T/\varepsilon_2 = \beta(1+\beta/4)$, $C = 1 + 4/\beta$ in the model of Huang and Rhys, $\varepsilon_T/\varepsilon_2 = \beta/(1-\beta)$ in the tangency model, and $\varepsilon_T/\varepsilon_2 = \beta$ in the Kubo model. For weak coupling we have $\varepsilon_T/\varepsilon_2 \approx \beta$, $C \approx 4/\beta$ for all models, and $\ln C > 2$ always in the tangency model. We assume hereafter that $\varepsilon_T \lesssim \varepsilon_z$. The electron-phonon coupling is frequently characterized in the literature by the Hyang-Rhys factor S. which is equal to the ratio of the polaron shift to the phonon energy $\hbar\omega_1$. It is connected with the introduced constant β by the relations $S\hbar\omega_1 = \varepsilon_T/C$ in the Huang-Rhys model and $S\hbar\omega_1 = \beta\varepsilon_T$ in the tangency model. Note that the expression "weak coupling" ($\beta \ll 1$) used here does not presuppose smallness of S.

To find the limits of the applicability of the linear dependence of τ on T^{-1} we obtain E_0 with the aid of Eq. (4). At small E the times τ_1 and τ_2 depend on E quite differently. As already mentioned, τ_2 is practically constant, but τ_2 has a logarithmic divergence due to the density of the barrier to the nucleus. Assuming $U_2 = M\omega^2 X^2/2$, we easily obtain $\tau_2 \approx (2\omega)^{-1}\ln(4\varepsilon_2/E)$, and Eq. (4) yields

$$E_0 = \frac{4\varepsilon_2}{C} \exp\left(-\frac{\hbar\omega}{k_B T}\right), \tag{12}$$

from which we see that $E_0 \ll \varepsilon_T > \varepsilon_2$, and consequently τ_{10} is

constant and equal to τ_0 [Eq. (11)] for $k_B T < \hbar\omega$. At very low temperatures, $k_B T < \hbar\omega/\ln(\varepsilon_T/\hbar\omega)$, E_0 becomes smaller than $\hbar\omega$. The saddle point in terms of E can not be used in this case and it must be assumed that $E_0 = \hbar\omega/2$. Nonetheless, relations (9)–(11) remain in force. In the case of weak coupling ($\beta \ll 1$), E_0 remains smaller than ε_2 (and the tunneling character of the transitions is preserved) also if $k_B T > \hbar\omega$. In this case, however, Eq. (12) becomes invalid. A more general expression for E_0 can be obtained by using the fact that at $E_0 < \varepsilon_2$ and for weak coupling the terms near the level E_0 take the form of almost parallel parabolas spaced vertically ε_T apart. An equation similar to that used above for τ_2 viz., $\tau_1 = (2\omega)^{-1}\ln[4\varepsilon_2/(E+\varepsilon_T)]$, can therefore be used for τ_1. Equation (4) yields then $E_0 = \varepsilon_T/[\exp(\hbar\omega/k_B T) - 1]$ (in accordance with Ref. 1), and we obtain

$$\tau = \frac{1}{2\omega} \ln\left[C\left(\exp\frac{\hbar\omega}{k_B T} - 1\right)\right]. \tag{13}$$

It can be seen that if $k_B T > \hbar\omega$ the temperature dependence of the time τ becomes weaker. Expression (13) for τ is valid so long as $E_0 \ll \varepsilon_2$, i.e., in the entire region $k_B T \ll \hbar\omega/\beta$.

In this region, the probability of thermoionization in a zero field[1,12,13] can be represented in the form

$$W_0 \propto \exp[-\theta(E_0, 0)], \quad \theta(E_0, 0) = \frac{\varepsilon_T}{\hbar\omega}[2\omega\tau - a], \tag{14}$$

where $a = 2$ in the tangency model, $a = 1 - C^{-1}$ in the Huang-Rhys model, and $a = 0$ in the Kubo model. It is seen from (13) and (14) that the choice of model for the terms at $k_B T < \hbar\omega/\beta$ influence the field and temperature dependences of the ionization probability only via the constants C and a.

The field dependences of (9) and (13) can be obtained from simple considerations. The probability $W(\varepsilon)$ of emission of an electron of energy ε can be estimated to be the product of the probability $n = (\varepsilon_T + \varepsilon)/\hbar\omega$ of absorption of vibrational quanta by the electron tunneling probability:

$$W(\varepsilon) \sim \left(\frac{1}{C}N_\omega\right)^n \exp\left(-\frac{4}{3}\frac{(2m)^{1/2}}{\hbar F}|\varepsilon|^{1/2}\right),$$

where $N_\omega = [\exp(\hbar\omega/k_B T) - 1]^{-1}$. Optimizing the exponent with respect to ε, we obtain Eqs. (9), (13), and (14) accurate to the term a. This derivation is due to Keldysh,[14] who obtained Eq. (9) at $\tau = \hbar/2k_B T$, corresponding to temperatures so low that τ_{10} in (6) can be neglected. Keldysh's result was later duplicated in Ref. 15.

At high temperatures, when $k_B T > \hbar\omega/\beta$ the optimal energy E_0 of the nucleus approaches the energy at which the terms ε_2 meet. Nonetheless, the exponential dependence of the transition probability $\exp[-2(s_2 - s_1)]$ is preserved so long as the difference between the actions is large. For the function $\theta(E,0)$ at $\varepsilon_2 - E \ll \varepsilon_2$ we get, using the equations of the Appendix,

$$\theta(E,0) = \frac{4}{3q}\left(\frac{\varepsilon_2 - E}{\varepsilon_s}\right)^q + \frac{E + \varepsilon_T}{k_B T}, \quad \varepsilon_s = \varepsilon_2\left(\frac{\eta\hbar\omega}{\varepsilon_T}\right)^{1/q}, \tag{15}$$

where $q = 5/2$, $\eta = 2/(1-\beta)$ for the tangency model,[1,16] $q = 3/2$, $\eta = 4/3(1+\beta/4) \times (1+\beta/2)$ for the Huang-

Rhys model, and $q = 3/2$, $\eta = 2/3(1 + \beta)$ for the Kubo model. From (15) we obtain the optimal value $(\varepsilon_2 - E_0)^{q-1} = 3/4\varepsilon_s^q/k_B T$, whence $W_0 \propto \exp[-\theta(E_0,0)]$,

$$\theta(E_0, 0) = \frac{\varepsilon_1}{k_B T} - \frac{4}{3} \frac{q-1}{q} \left(\frac{3}{4} \frac{\varepsilon_s}{k_B T} \right)^{q/(q-1)} \quad (16)$$

where ε_1 is the energy at which the terms U_1 and U_2 meet and is reckoned from the bottom of the term U_1. The first term of (16) corresponds to the classical thermoactivation dependence of the transition probability, but the second term, so long as it is large (so long as $k_B T < \varepsilon_s$), increases substantially the ionization probability on account of the tunneling of the nucleus.

We now obtain for $k_B T > \hbar\omega/\beta$ the value of τ in Eqs. (7)–(9). At $\varepsilon_2 - E_0 \ll \varepsilon_2$ we have according to (A.2) $\omega\tau = [(\varepsilon_2 - E_0)/\varepsilon_2]^{1/2}$, whence

$$\tau = \frac{\hbar(2+\beta)}{2\beta k_B T}, \quad \tau = \frac{\hbar(1+\beta)}{2\beta k_B T}, \quad \tau = \frac{1}{\omega}\left(\frac{3}{2} \frac{\hbar\omega}{\beta k_B T} \right)^{1/3}, \quad (17)$$

Respectively for the Huang-Rhys, Kubo, and tangency models. The first equation of (17) agrees with the Timashev's result.[5]

The field dependence of the ionization probability in weak fields is thus given by Eq. (9), in which τ is determined by Eq. (13) if $k_B T < \hbar\omega/\beta$ and by (17) if $k_B T > \hbar\omega/\beta$.

For the Huang-Rhys model we can deduce, using Eq. (25) below, expressions that are valid in the entire temperature interval:

$$\theta(E_0, 0) = \frac{\varepsilon_T}{\hbar\omega} \left[2\omega\tau - (1 + \xi_0^2)^{1/2} + \frac{1}{C} \coth \frac{\vartheta}{2} \right],$$

$$2\omega\tau = \frac{\vartheta}{2} + \ln \frac{1 + (1 + \xi_0^2)^{1/2}}{\xi_0},$$

$$\xi_0 = \frac{1}{C \sh(\vartheta/2)}, \quad \vartheta = \frac{\hbar\omega}{k_B T}.$$

We ascertain now the conditions under which Eqs. (8) and (9) are valid, i.e., the field can be regarded as weak. In models with crossing terms, the corresponding criterion coincides with the condition that the field term in (8) be small[1)] compared with $\theta(E,0)$:

$$F \ll F_0/2\omega\tau, \quad F_0 = 2(2m\varepsilon_T)^{1/2}\omega. \quad (18)$$

The characteristic force F_0 corresponds to the field for which the electron tunneling time from a state with binding energy ε_T becomes of the order of the period of the nucleus vibrations. The condition (18) means simultaneously that the optimal energy of the emitted electon is $|\varepsilon_0| \ll \varepsilon_T$ (since the equation $|\varepsilon_0| = F^2\tau^2/2m$ can be rewritten in the form $|\varepsilon_0| = \varepsilon_T (F/F_0)^2 (2\omega\tau)^2$).

In the term-tangency model the condition for the validity of (8) at $k_B T < \hbar\omega/\beta$ is also given by the inequality (18). At $k_B T > \hbar\omega/\beta$, however, it can be shown that (8) is valid only up to fields $F < F_0(1 - \beta)^{1/2}\omega\tau/2$ (note that $\omega\tau < 1$ here). In stronger fields, while $|\varepsilon_0|$ remains smaller than ε_T, the field dependence of W is altered by the influence of the field on the optimal energy E_0 of the nuclear transition. The

corresponding relation (24) will be obtained below.

2. We proceed to consider strong fields, when the optimal energy $|\varepsilon_0|$ of the emitted electron approaches ε_T. Using (4) and (5) we readily verify that this energy becomes equal to ε_T at[2)] $F/F_0 \approx 2k_B T/\hbar\omega$. In stronger fields, the bottom of the term U_{ε_0} drops below the bottom of U_1. The ionization of a center in weak fields can be regarded as thermoionization facilitated by the field. In strong fields, on the contrary, the ionization has in the main the character of cold emission influenced by the interaction between the electron and the vibrations of the nucleus. This interaction necessitates corrections to the principal field exponent of the exponential $\Phi_c \sim (2m)^{1/2}\varepsilon_T^{3/2}/\hbar F$, due to tunneling of the electron through a triangular barrier. In very strong fields, the optimal energy ε_0 is determined entirely by the most favorable conditions for the nuclear transition. Under these conditions the term U_ε lies lower than U_1, so that the terms cross at the minimum point of U_1 (Fig. 1, curve 2). The cold-ionization probability is, with exponential accuracy,

$$W \propto \exp[-\tfrac{4}{3}(2m)^{1/2}\varepsilon_f^{3/2}/\hbar F]. \quad (19)$$

The "field binding energy" ε_f exceeds the thermal energy. This effect is similar to the known difference between the optical (ε_{opt}) and thermal (ε_T) binding energies. It can be seen from Fig. 1 that in the Huang-Rhys model $\varepsilon_f = \varepsilon_T(1 + C^{-1})$, and in the tangency model $\varepsilon_f = \varepsilon_T/(1 - \beta)$.

If the binding energy is comparable with the band gap E_g, the electron-tunneling probability cannot be calculated in the effective-mass approximation, and account must be taken of the true energy spectrum $\varepsilon(k)$ in the forbidden band (at imaginary k). In the Kane model, for example, ε_f in (19) must be replaced by ε_f^*, where

$$(\varepsilon_f^*)^{3/2} = \tfrac{3}{8}\varepsilon_g^{3/2}\{\arcsin(u^{1/2}) - (1-2u)[u(1-u)]^{1/2}\}, \quad u = \varepsilon_f/E_g.$$

Let us find the corrections to the argument of the exponential (19). At $|\varepsilon|$ close to ε_f, the barrier to tunneling by the nucleus is due almost entirely to the action s_1. The nuclear transition probability is therefore determined by the probability of finding the nucleus on the parabola U_1 at the point of term crossing. Then

$$\theta(E_0, \varepsilon) = 2 \frac{\tilde{\varepsilon}_1}{\hbar\omega_1} \th \frac{\hbar\omega_1}{2k_B T}, \quad (20)$$

where $\tilde{\varepsilon}_1$ is the energy distance from the bottom of the parabola U_1 to the crossing point of terms U_1 and U_ε. The connection between $\tilde{\varepsilon}_1$ and ε for different models is given in the Appendix. Equation (20) can be obtained also from the explicit expressions (A.1) for s_1 and s_2. Optimizing the function $\Phi(E_0,\varepsilon)$ with respect to ε at $\varepsilon_f - |\varepsilon| \ll \varepsilon_f$ we get $W \propto \exp(-\Phi_c)$, with

$$\Phi_c = \frac{4}{3} \frac{(2m)^{1/2}}{\hbar F} \varepsilon_f^{3/2} - b \frac{m\omega_1}{\hbar} \frac{\varepsilon_f^2}{F^2} \cth \frac{\hbar\omega_1}{2k_B T}, \quad (21)$$

where $b = 4/(C + 1)$ in the Huang-Rhys model and $b = 4\beta/(1 - \beta)$ in the tangency model. Equation (21) describes the effect of interaction with local vibrations on cold ionization of the center by a strong electric field. If

$k_B T < \hbar\omega$, it is valid under the condition $F > F_0$. If account is taken of the Kane spectrum, ε_f in the first term of (21) is replaced by ε_f^*, while b is replaced by $b^* = b(1 - \varepsilon_f/E_g)$.

At $k_B T > \hbar\omega/\beta$ we can write down expressions that are valid for the entire range of electric fields, from weak to strong. The reason is that at high temperature the transition of the nucleus between the terms U_1 and U_ε occurs at an energy close to the term crossing. It can therefore be assumed that

$$\Phi(E_0, \varepsilon) = \bar{\varepsilon}_1/k_B T + 4(2m)^{1/2}|\varepsilon|^{3/2}/3\hbar F.$$

(This approach was used in Refs. 5, 7, and 10.) After determining the minimum of the function $\Phi(E_0,\varepsilon)$ with respect to ε, we readily obtain:

a) For the Huang-Rhys model

$$W \propto \exp(-\Phi_c),$$

$$\Phi_c = \frac{8}{3}\frac{\bar{\varepsilon}_1}{k_B T}\tilde{F}^{-4}[(1+\tilde{F}^2)^{1/2}-1]^2\left[(1+\tilde{F}^2)^{1/2}+\frac{1}{2}\right], \quad (22)$$

$$\tilde{F} = (C^2+C)^{1/2}\frac{\hbar\omega}{k_B T}\frac{F}{F_0}.$$

This expression goes over into Eq. (21) at $\tilde{F} \gg 1$ and into Eq. (8) at $\tilde{F} \ll 1$.

b) For the term-tangency model

$$W \propto \exp(-\Phi_c),$$

$$\Phi_c = \frac{\bar{\varepsilon}_1}{k_B T}\tilde{F}^2[(1+\tilde{F}^{-1})^{1/2}-1]^3\left[(1+\tilde{F}^{-1})^{1/2}+\frac{1}{3}\right], \quad (23)$$

$$\tilde{F} = (1-\beta)^{3/4}\frac{\hbar\omega}{4\beta k_B T}\frac{F}{F_0}.$$

This equation is valid for $F > F_0\omega\tau(1-\beta)^{1/2}/2$. At $\tilde{F} \gg 1$ it goes over into (21), while at $\tilde{F} \ll 1$ it yields

$$\Phi_c = \frac{\bar{\varepsilon}_1}{k_B T}\left(1 - \frac{8}{3}\tilde{F}^{1/2}\right). \quad (24)$$

Figure 3 shows those regions of the (T,F) plane in which the relations derived above are valid.

In the Huang-Rhys model it is possible to obtain for E_0 an explicit expression.[17] We can then write for arbitrary fields
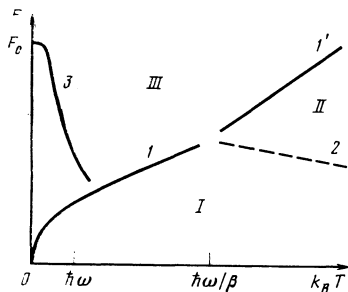
FIG. 3. Schematic representation of the regions of applicability of different theoretical equations for the ionization probability of the center: I—Eqs. (9), (13), (14) for $k_B T < \hbar\omega/\beta$, and (9), (16), (17) for $k_B T > \hbar\omega/\beta'$; II—(24) for the tangency model and (9), (16), (17) for the Huang-Rhys and Kubo models; III—(21). The tentative boundaries of the regions are determined by the curves: $1 - F = F_0/2\omega\tau$; $1' - F = F_0\beta k_B T/2\hbar\omega(1-\beta)^{1/2}$; $2 - F = F_0\omega\tau(1-\beta)^{1/2}/2$; $3 - F = F_0\tanh(\hbar\omega/2k_B T)$.
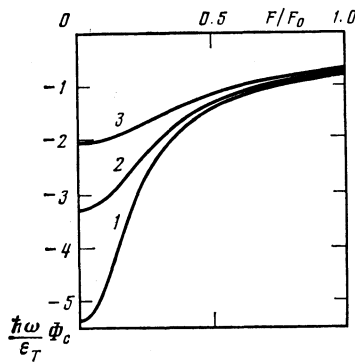
FIG. 4. Field dependence of the argument of the exponential of the center-ionization probability $W \propto \exp(-\Phi_c)$ in the Huang-Rhys model ($C = 10$) at various temperatures: $1 - k_B T = 0.25\hbar\omega$; $2 - k_B T = 0.5\hbar\omega$; $3 - k_B T = \hbar\omega$.

$$\frac{\hbar\omega}{\varepsilon_T}\Phi_c = |1-y|\left[\pm 2\omega\tau(y) - (1+\xi^2)^{1/2}+\xi\,\mathrm{ch}\frac{\vartheta}{2}\right] + \frac{2}{3}\frac{F_0}{F}y^{3/2}, \quad (25)$$

$$2\omega\tau(y) = \frac{\vartheta}{2}\pm\ln\frac{1+(1+\xi^2)^{1/2}}{\xi}, \quad \xi = \frac{1}{C|1-y|\mathrm{sh}(\vartheta/2)},$$

$$\vartheta = \frac{\hbar\omega}{k_B T}, \quad y = \frac{|\varepsilon_0|}{\varepsilon_T},$$

where the upper and lower signs correspond to the cases $y < 1$ and $y > 1$, while y is the solution of the equation

$$(F_0/F)y^{1/2} = 2\omega\tau(y). \quad (26)$$

Figure 4 shows an example of the calculation of the argument of the exponential in the ionization probability $W \propto \exp(-\Phi_c)$ in accordance with Eqs. (25) and (26).

§2. CALCULATION OF THE COEFFICIENT OF THE EXPONENTIAL

We calculate the probability of electron transition from a bound to a free state by perturbation theory, using the nonadiabaticity operator as the perturbation. The corresponding calculation in a zero field leads in the limiting cases only to a small numerical difference (Ref. 1) from the exact results. We calculate first the electron matrix element

$$M_{1k} = \int d^3r\,\psi_1^*(\mathbf{r}, X)\frac{\partial}{\partial X}\psi_k(\mathbf{r}, X). \quad (27)$$

Here ψ_1 and ψ_k are wave functions corresponding to the bound and free states of the electron, and in which the coordinate X of the nucleus enters as a parameter. We assume that the potential of the center has a zero radius.[16] The electron wave functions satisfy then in the presence of an external field the relation (in atomic units)

$$[-\tfrac{1}{2}\Delta+V(\mathbf{r})-\varepsilon]\psi=0, \quad (28)$$

with the boundary condition

$$\left[\left(\frac{\partial}{\partial r}r\psi\right)\bigg/(r\psi)\right]_{r\to 0} = -\varkappa, \quad (29)$$

where $v(\mathbf{r})$ is the potential energy of the electron in an exter-

nal field, $\varkappa = (2m\varepsilon_x)^{1/2}$, and ε_x is the binding energy at $V = 0$. The wave function ψ_1 of the bound state is equal, apart from a factor, to the Green's function of (28): $\psi_1 = C_1 G_1(\mathbf{r})$, where C_1 is a normalization constant and G_1 satisfies the equation

$$[-\tfrac{1}{2}\Delta + V(\mathbf{r}) + \varepsilon_b] G_1 = \delta(\mathbf{r}).$$

The binding energy ε_b is determined from the boundary condition

$$\varkappa + 2\pi \left[\frac{\partial}{\partial r}(rG_1) \right]_{r \to 0} = 0.$$

It is assumed that the quantity dependent on the position X of the nucleus is only the short-range part of the potential, i.e., $\varkappa$ and hence ε_b. The wave function of the free state can be written in the form

$$\psi_k = \psi_k^{(0)}(\mathbf{r}) + C_k G_k(\mathbf{r}),$$

where $\psi_k^{(0)}$ is a function of the continuum without allowance for the short-range potential, and G_k is a Green's function satisfying the equation

$$[-\tfrac{1}{2}\Delta + V(\mathbf{r}) - \varepsilon_k] G_k = \delta(\mathbf{r}).$$

The coefficient C_k is determined from the boundary condition (29)

$$C_k = -\frac{2\pi\psi_k^{(0)}(0)}{\varkappa(1+\gamma)}, \qquad \gamma = \frac{2\pi}{\varkappa}\left[\frac{\partial}{\partial r}(rG_k) \right]_{r \to 0}.$$

It can be seen that the function ψ_k depends on $\varkappa$, meaning also on the coordinate X of the nucleus, only via the coefficient C_k. For M_{1k} we obtain

$$M_{1k} = \frac{2\pi C_1^* \psi_k^{(0)}(0)}{\varkappa^2(1+\gamma)^2} J \frac{d\varkappa}{dX}, \qquad J = \int d^3r\, G_1^* G_k. \tag{30}$$

To calculate the integral J, we multiply the equation for G_1^* by G_k and the equation for G_k by G_1^*, subtract one from the other, and integrate over d^3r. We then obtain

$$J = \frac{1}{\varepsilon_b^* + \varepsilon_k}[G_k(\mathbf{r}) - G_1^*(\mathbf{r})]_{r \to 0}.$$

The expansion of the Green's functions at small r begins with the term $(2\pi r)^{-1}$, and the last expression can therefore be rewritten as

$$J = \frac{1}{\varepsilon_b^* + \varepsilon_k}\left[\frac{\partial}{\partial r}(rG_k) - \frac{\partial}{\partial r}(rG_1^*) \right]_{r \to 0} = \frac{\varkappa}{2\pi}\frac{1+\gamma}{\varepsilon_b^* + \varepsilon_k}.$$

Substituting this expression in (30), we get

$$M_{1k} = \frac{C_1^* \psi_k^{(0)}(0)}{\varkappa(1+\gamma)(\varepsilon_b^* + \varepsilon_k)}\frac{d\varkappa}{dX}. \tag{31}$$

In a weak electric field this expression simplifies substantially. The influence of the field need be taken into account only in the continuum wave function. Then $C_1 = (2\pi\varkappa)^{1/2}$ and we can neglect ε_k and γ in the denominator, so that

$$M_{1k} = 2(2\pi)^{1/2}\psi_k^{(0)}(0)\,\varkappa^{-5/2}d\varkappa/dX.$$

Using this expression for the matrix element and calculating the transition probability in analogy with Ref. 1, we get

$$W = W_0 I, \qquad I = \sum_k \left(\frac{4\pi\hbar\tau}{m} \right)^{3/2} |\psi_k^{(0)}(0)|^2 \exp\left(-\frac{2\tau\varepsilon_k}{\hbar} \right), \tag{32}$$

where W_0 is the thermoionization probability in a zero field.

In an electric field we have

$$\psi_k^{(0)}(\mathbf{r}) = \psi_{\varepsilon_\parallel}(z)L^{-1}\exp(i\mathbf{k}_\perp \boldsymbol{\rho}),$$

where $\varepsilon_\parallel$ is the energy of motion along the field, $\mathbf{k}_\perp$ is the transverse vector, and L is the renormalization length. Integrating with respect to $\mathbf{k}_\perp$ we obtain

$$I = \left(\frac{4\pi\hbar\tau}{m} \right)^{1/2} \int_{-\infty}^{\infty} d\varepsilon_\parallel \exp\left(-\frac{2\tau\varepsilon_\parallel}{\hbar} \right) |\psi_{\varepsilon_\parallel}(0)|^2.$$

Here $\psi_{\varepsilon_\parallel}(z)$ is an Airy function normalized to $\delta(\varepsilon_\parallel - \varepsilon_\parallel')$. The integral with respect to $\varepsilon_\parallel$ can be evaluated exactly, and it turns out as a result that $I = \exp(F^2\tau^3/3\hbar m)$, while for the ionization probability we obtain Eq. (9). The approximations made are valid if the characteristic energy of the emitted electron $|\varepsilon_0| = F^2\tau^2/2m$ is small compared with the characteristic binding energy $\Delta\varepsilon_b$, which is determined by the width of the saddle in the calculation of the integral with respect to the nuclear coordinate X in the matrix element of the transition. For the tangency model we have $\Delta\varepsilon_b = [9\beta(\varepsilon_2 - E_0)(\hbar\omega)^2]^{1/3}$, and for the Huang-Rhys and Kubo models $\Delta\varepsilon_b = [4\beta^2\varepsilon_2 - E_0)(\hbar\omega)^2]^{1/4}$.

We present also an expression for W_0 at $k_B T < \hbar\omega/\beta$ in the tangency model[1]:

$$W_0 = \omega\left(\frac{4}{C\beta} \right)^{1/2} \frac{A}{(2\omega\tau)^{1/2}}\frac{\mathrm{sh}(\hbar\omega_1/2k_B T)}{\mathrm{sh}(\hbar\omega/2k_B T)}\exp[-\theta(E_0,0)],$$

$$A = \frac{16}{2^{1/2}\cdot 27},$$

where the principal term of the argument of the exponential $\theta(E_0,0)$ is given by Eq. (14).

We proceed now to the case of strong electric fields (at $k_B T < \hbar\omega$ this is the field region $F > F_0$). Nonetheless, the fields are still assumed to be weak enough for the argument $4(2m)^{1/2}\varepsilon_T^{3/2}/3\hbar F$ of the tunnel exponential to be large. It can be shown here[16] that $\gamma = -(|\varepsilon_k|/\varepsilon_b)^{1/2}$ in expression (31). In a strong field the term-crossing point X_ε is located between the turning points. Using quasiclassical vibrational wave functions of the nucleus and recognizing that the main contribution to the exponential is made by the vicinity of the point X_ε we obtain for the matrix element of the transition

$$V_{1k} = -\frac{\hbar(\omega_1\omega)^{1/2}}{2\pi}\exp[-(s_1 - s_2)]$$

$$\times \int dX M_{1k}(X)\exp[-\nu(X - X_\varepsilon)^2]. \tag{33}$$

Here $\nu = |(2\hbar)^{-1}[M/2(\tilde{\varepsilon}_1 - E_1)]^{1/2}d\varepsilon_b/dX|_{x=x\varepsilon}$. The integral is evaluated along the real axis, the singularity of M_{ik} is located at $X = X_\varepsilon + i\delta$, and the small imaginary part δ is due to the weak nonstationarity of the bound state. Calculation, using (33), of the probability of ionization by a strong field yields

$$W = [F/2(2m\varepsilon_f)^{1/2}]\exp(-\Phi_c), \tag{34}$$

where ε_f is the field binding energy, and the principal part of Φ_c is given by (21). Note that in the strong-field limit the use of the nonadiabaticity operator as a perturbation yields not only the correct argument of the exponential, but also the correct prefactor that coincides with the result of Demkov and Drukarev.[18]

§3. COMPARISON WITH EXPERIMENT

The data of Sah's group[3,4,19] on thermoionization of deep centers in silicon pertain to fields that are weak (as defined in the present article). A quadratic field dependence of the logarithm of the ionization probability obtains for many deep centers (Au, Ag, Zn, Co, radiation defects). Reference 2 contains a detailed discussion of the data on thermoemission electrons and holes from an acceptor level of gold, and it is shown there that these data are well described by relations (9) and (10) for τ_0 independent of temperature. This shows that under the experimental conditions we have $k_B T < \hbar\omega$ and $\tau_0 = \ln C /2\omega$ in accordance with (11). The experimental data on thermoemission of electrons yielded $\hbar\omega/k_B \ln C \approx 410$ K. It can therefore be assumed that $\hbar\omega/ k_B \sim 10^3$ K. This permits an estimate of the characteristic field $F_0 = 2(m\varepsilon_T)^{1/2}\omega$. It turns out that $F_0 \approx 4\cdot10^6$ eV/cm. The maximum $\omega\tau$ in the experiment is approximately four. Therefore, according to criterion (18), a quadratic dependence of $\ln W$ on the field can be expected up to fields $F < 5\cdot10^5$ eV/cm. In the experiments of Sah and co-workers[3,4,19] the fields used were up to $F \approx 1.5\cdot10^5$ eV/cm. In Ref. 20 are given data for electron thermoemission from the same level of gold in fields up to $F \approx 5.5\cdot10^5$ eV/cm. Figure 5, in which these data are shown in appropriate scale, show that the linear dependence of $\ln W$ on F^2 is preserved almost in this entire field interval. Figure 6 shows the temperature dependence of the time τ (at $m = 0.33\,m_e$), determined from these data, together with the data of Ref. 3. The slope of the lines agrees with the theory [Eq. (10)]. The

FIG. 6. Dependence of the time of nucleus tunneling on the reciprocal temperature for ejection of electrons from a gold acceptor level in silicon, determined from the data of Refs. 3 (●) and 20 (○).

value $\hbar\omega/k_B \ln C \approx 960$ K from the data of Ref. 20 differs from the value ≈ 410 K from the data of Ref. 3.

The authors of Ref. 20 reduced their data by using the equations of Makram-Ebeid and Lannou.[9] This data reduction yielded unrealistic values of the parameters, particularly of the energy $\hbar\omega/k_B \approx 110$ K. The reason, in our opinion, is that these equations do not hold in weak fields.

For gallium arsenide, owing to the lower oscillation frequency and the small effective mass of the electron, it can be assumed that the characteristic field E_0 will be of the order of 10^5 eV/cm. Therefore the experimental data of Ref. 9, in which $F \approx (1-4)\cdot10^5$ eV/cm, pertain apparently to the region of intermediate or strong fields. This is attested also by the observed sublinear dependence of $\ln W$ on F (see Fig. 4 for comparison).

APPENDIX

In the considered models of the adiabatic terms, the expressions for the actions and the tunneling times of the nucleus are of the form

$$s_i = \frac{\bar\varepsilon_i}{\hbar\omega_i}z_i^{1/2} - \frac{E_i\tau_i}{\hbar}, \qquad \tau_i = \frac{1}{2\omega_i}\ln\frac{1+z_i^{1/2}}{1-z_i^{1/2}},$$

$$z_i = 1 - \frac{E_i}{\bar\varepsilon_i}, \qquad i=1,2, \tag{A.1}$$

where $\bar\varepsilon_1$ and $\bar\varepsilon_2$ are the crossing energies of the terms U_1 and U_2, and $E_1 = E_2 = E$ are the nuclear vibration energies. The energies $\bar\varepsilon_1$ and E_1 are measured from the bottom of the term U_1, and $\bar\varepsilon_2$ and E_2 from the bottom of U_2, while ω_1 and $\omega_2 = \omega$ are the frequencies of the vibrations on the terms U_1 and U_2, respectively. At low $z_1 \ll 1$ we have the asymptotic expressions

$$s_i = \frac{\bar\varepsilon_i}{\hbar\omega_i}\left[\frac{2}{3}z_i^{3/2} + \frac{2}{15}z_i^{5/2} + \dots\right], \qquad \tau_i \approx \frac{1}{\omega_i}z_i^{1/2}. \tag{A.2}$$

The term-crossing energies are connected with the energy of the emitted electron $y \equiv |\varepsilon|/\varepsilon_T$ by the following relations:

1) in the term-tangency model

$$\varepsilon_1 = \frac{\varepsilon_T}{\beta}[1 - (1-\beta)^{1/2}y^{1/2}]^2, \qquad \bar\varepsilon_2 = \frac{\varepsilon_T}{\beta}[(1-\beta)^{1/2} - y^{1/2}]^2, \tag{A.3a}$$
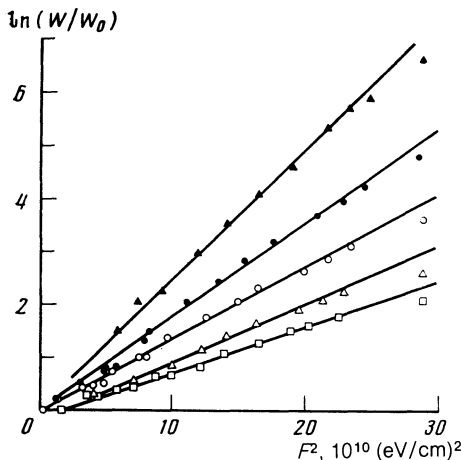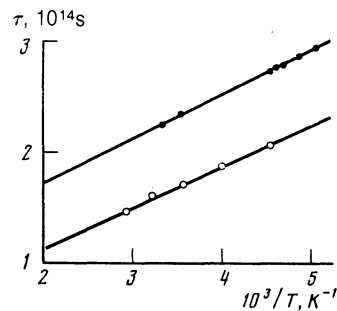
2) in the Huang-Rhys model

FIG. 5. Dependence of the logarithm of the probability of electron thermoemission from a gold acceptor level in silicon[20] on the square of the electric field at various temperatures: ▲ — 220 K; ● — 250 K; ○ — 280 K; △ — 310 K; □ — 340 K.

$$\bar{\varepsilon}_1 = \varepsilon_T \frac{C}{4} \left[1 + \frac{1}{C} - y \right]^2, \qquad \bar{\varepsilon}_2 = \varepsilon_T \frac{C}{4} \left[1 - \frac{1}{C} - y \right]^2,$$

$$C = \frac{4}{\beta} + 1, \tag{A.3b}$$

3) in the Kubo model

$$\bar{\varepsilon}_1 = \frac{\varepsilon_T}{\beta}(1+\beta)(1-y), \qquad \bar{\varepsilon}_2 = \frac{\varepsilon_T}{\beta}(1-y). \tag{A.3c}$$

[1] Note that condition (18) means that the term quadratic in the field in (8) is the principal one in the field dependence of the logarithm of the thermoionization probability. The condition under which the corrections to the quadratic term of (8) in the argument of the exponential are less than unity is more stringent than (18) and is given in §2.

[2] The vicinity of the point $F/F_0 = 2k_B T/\hbar\omega$ was investigated in detail by Dalidchik.[8]

[3] Note that Eq. (32) is valid for any external sufficiently smooth potential $V(\mathbf{r})$ (particularly a Coulomb potential), when its influence on the bound state can be neglected and when the characteristic energy of the emitted electron is $|\varepsilon_k| \ll \Delta\varepsilon_b$.

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