Multiphonon tunnel processes in a homogeneous electric field

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(Submitted 24 June 1977)
Zh. Eksp. Teor. Fiz. 74, 472–482 (February 1978)

The problem of electrophotodisintegration of molecules and impurity centers in crystals, followed by emission and absorption of vibrational quanta (phonons), is solved analytically for the principal model of multiphonon transitions. Limiting cases are considered, limits are established for the applicability of the approximate expressions, and the singularities in the manifestation of the vibronic interaction in strong and weak fields are elucidated. Field-induced disintegration of impurity centers of doped luminors is used as an example in a comparison between theory and experiment. The dependence of the field intensity on the applied voltage and estimates of the electron-vibrational interaction are obtained for ZnS:(A), where A = Cu, Ag, and Pb.

PACS numbers: 78.50.—w, 63.20.Mt

1. INTRODUCTION

Multiphonon processes that accompany optical transitions of localized electrons determine the main features of the absorption and luminescence spectra of impurity crystals. These processes have been diligently studied starting with the known papers of the Fifties, and abundant experimental and theoretical material has by now been accumulated.[1,2] similar problems are being solved also in connection with the electron-vibrational interaction in polyatomic molecules.[3] A characteristic feature of the mentioned processes is that the electron matrix elements that enter in the calculated quantities are independent of energy. An energy dependence appears, obviously, in the case of electron detachment.

The influence of the electron-vibrational interaction on photodisintegration (ionization) processes was investigated in[4-7]. It was established that energy exchange between the released electron and the vibrational degrees of freedom alters noticeably the frequency dependences of the photoionization, which are used in practice for spectroscopic purposes.

The dynamic coupling with the vibrational subsystem is even more significant for processes that include a stage of slow tunneling of an electron—field-induced ionization of molecules and impurity centers, as well as in the case of low-frequency electro-absorption. If the electric field is strong and the condition $\omega|\tau|\ll 1$ is satisfied (ω is the characteristic oscillation frequency of the nuclear subsystem and τ is the imaginary tunneling time), the electron detachment is an instantaneous process relative to the vibrational degrees of freedom, and the electron-vibrational coupling is negligible.1) Under these conditions the field-induced ionization and the electro-absorption of multicenter systems are described by the formulas previously derived in[8,9]. The situation is qualitatively different in weaker fields $\omega|\tau|\gtrsim 1$, for which the presence of pronounced temperature dependences has been established.[10-15] This is evidence that in this case the outward tunneling of the electron is connected with the production and absorption of vibrational quanta (phonons).

Single-phonon processes that accompany interband tunneling of an electron in an electric field were taken into account by Keldysh.[16] Multiphonon processes that occur in electro-optical disintegration of impurity levels were considered phonomenologically by Timashev[17-18] and Kudzhmauskas.[13,19] In these papers they used essentially for the optical-absorption line shape (for the distribution function of the vibrational transitions), a quasiclassical (Gaussian) approximation for which there is a well-known applicability condition:

$$n=(e^{\omega/T}-1)^{-1}\gg 1. \tag{1}$$

(Here T is the system temperature, and n are the equilibrium occupation numbers of the normal oscillators. We use $e=h=m=k=1$ throughout.)

The condition (1) is not satisfied in the published experiments.[10-15] For optical transitions, which correspond to a larger heat release, the Gaussian approximation of the true line shape can be used (in the fundamental frequency region) also if $T\sim\omega$. For tunnel processes, however, which are characterized by an exponential dependence of the decay rate on the energy of the released electrons, this approximation not only lacks a methodological foundation, but is inapplicable in a number of cases from physical considerations. It is obvious that in a sufficiently weak field, and also in the case of low temperatures, the energy spectrum of the emitted electrons corresponds not to a normal but to a Poisson distribution of the vibrational transitions. In fact, in the former case penetration of the electron through the field barrier is possible only after absorption of a sufficient number of vibrational quanta, a number that can exceed the average value typical of non-tunneling optical transitions. At $n\ll 1$, on the contrary, the emission of the electron is inevitably accompanied by excitation of vibrational degrees of freedom, and here the situation is similar to the one known in quantum electrodynamics,[20] p. 449 [p. 350 of translation]. The average energy of the released electrons depends in a complicated manner on all the energy parameters of the system: the electron binding energy Δ, the temperature T, the constant-electric field intensity

0038-5646/78/4702-0247$02.40

F, the frequency ω of the vibrational quantum, and the electron-vibrational interaction constant a (the Stokes-loss parameter). The solution of the problem must thus not depend on some particular approximation of the distribution function of the vibrational transitions. It is shown below that within the framework of the principal model[2,3] it becomes possible to obtain for the electro-optical disintegration probability a single analytic expression (formula (13)) that admits of a lucid interpretation and makes it possible to trace transitions to all possible particular and limiting cases. These cases are analyzed in Sec. 3. Theory and experiment are compared in Sec. 4.

2. FORMULATION OF PROBLEM. GENERAL SOLUTION

We consider multiphonon processes that accompany the electrophotodisintegration of molecular systems and impurity centers of crystals. The experimentally observable quantities, such as the coefficients of electro-absorption of light,[10] the intensity of the electroluminescence flash,[11-15] and the current pulse at the instant when the field is turned on[15] are proportional to the summary averaged electron-detachment rate $\overline{W}(T,F)$, the calculation of which is the main task of the theory.

In accord with the general formulation of the problem of multiphonon transitions we have

$$\overline{W}(T,F)=\sum_{\{n_i\}}\sum_{\{n_f\}}\prod_s P_s(n_s^i)\,|\langle n_s^i|n_s^f\rangle|^2 W(\varepsilon,F). \tag{2}$$

Here $\epsilon=\Omega+\sum_s\omega_s(n_s^i-n_s^f)$,

$$W(\varepsilon,F)=2\pi\int d\varkappa\, dE_z|\langle i|\mathbf{fr}|\varkappa E_z\rangle|^2\delta\left(\Delta+\varepsilon-\frac{\varkappa^2}{2}-E_z\right) \tag{3}$$

is the electronic factor of the disintegration rate, $\langle n_s^i|n_s^f\rangle$ are the overlap integrals (the Franck-Condon factors) of the wave functions of the normal oscillators, $\prod_s P_s(n_s^i)$ is the distribution function over the vibrational levels n_s^i in the initial state, s is the index of the normal coordinate, and the summation is over all possible combinations of the vibrational quantum number. We consider below the principal model of multiphonon transitions.[2,3] Allowance for the frequency effect, anharmonicity, degeneracy, and the more complicated dispersion law of the states of the electron continuum is of independent interest and requires a separate analysis.

In formula (3), $\mathbf{r}$ is the electron radius vector, $\mathbf{f}$ is the intensity of the light-wave field, Ω is the photon frequency, $|i\rangle$ is the wave function of the localized electron, and $|\varkappa,E_z\rangle$ is the wave function of a free electron in a uniform electric field ($\varkappa$ is the transverse momentum and E_z is the longitudinal energy). For the sake of argument we confine ourselves to the case of longitudinal polarization of the light ($\mathbf{f}\,||\,\mathbf{F}$). Formula (2) contains, as a particular case, also the rate of disintegration of the system by a constant field. To find this rate it suffices to put $\Omega=0$ and replace intensity of the electromagnetic wave by intensity F of the constant field. We put

$$|i\rangle=Ae^{-\alpha r}/r,\quad \alpha^2=2\Delta,$$

i.e., we shall treat systems of the negative-ion type.[2]

The problem is solved in two stages—calculation of the function $W(\epsilon,F)$ and subsequent summation over the vibrational quantum numbers. The electron factor is not calculated analytically in the usual case. It can be shown that at $\epsilon=0$ (elastic tunneling) the calculation of the function $W(0,F)$ reduces to the construction of the imaginary part of the field Green's function. This problem was solved in[8,21]. In another limiting case, when the elastic-decay channel is ineffective ($\epsilon\gg\sqrt{\alpha F}$), the electron factors can be found from the formulas of [9]. At arbitrary ϵ, the function $W(\epsilon,F)$ can be calculated asymptotically, in a higher-order approximation in terms of the small parameter $F(\Delta-\Omega)^{-3/2}$. It must be emphasized that this is the only case of interest for all the processes considered below. In fact, for the case of electro-absorption, the inequality $F\ll(\Delta-\Omega)^{3/2}$ determines the necessary condition for observing the most interesting (exponential) temperature and field effects. For field ionization, the condition $F\ll\Delta^{3/2}$ is implied already in the formulation of the problem.

Integrating with respect to the transverse coordinates and taking into account the equation of motion in a uniform field, we express the electronic matrix element in the form

$$\langle i|\mathbf{fr}|\varkappa E_z\rangle=N_j(\alpha/2\pi)^{1/2}J(\alpha^2+\varkappa^2,E_z,F), \tag{4}$$

$$J(\alpha^2+\varkappa^2,E_z,F)=\left(\frac{E_z}{F}+\frac{F}{2}\frac{d^2}{dE_z^2}\right)\int_{-\infty}^{\infty}dZ\,G^0(-(\alpha^2+\varkappa^2);0,Z)\,V\left(-\frac{2(E_z+FZ)}{(2F)^{2/3}}\right). \tag{5}$$

Here $N_j^2=(2\pi^3(2F)^{1/3})^{-1}$ is the normalization factor of the function $|\varkappa E_z\rangle$, and $G^0(-(\alpha^3+\varkappa^2);0,Z)$ is the one-dimensional Green's function of the free motion. We use the integral representation of the Airy function ([22], p. 736) and shift the integration contour to the upper half-plane to make it pass through the point $i\sqrt{x}$ ($x=-2E_z/(2F)^{2/3}\gg1$. We omit small terms ($\sim x^{-3/4}$) and carry out the rest of the integration exactly. The result is

$$\langle i|\mathbf{fr}|\varkappa E_z\rangle=-iN_j(\alpha/2)^{1/2}e^{-2/3x^{3/2}}\left(\frac{\sqrt{\pi}}{x^{1/4}}-\frac{\pi\gamma}{2x^{1/2}}e^{\gamma^2/4x^{1/2}}\left(1-\Phi\left(\frac{\gamma}{2x^{1/4}}\right)\right)\right). \tag{6}$$

Here $\gamma=2\epsilon/(2F)^{2/3}$, $\Phi(\xi)$ is the error integral, and $\xi=\epsilon/(2F)^{1/2}(-2E_z)^{1/4}$.

When integrating with respect to $\varkappa$ and E_z in (3) we recognize that the exponential factor varies rapidly over distances $F\Delta^{-1/2}$, whereas the remaining part of the function $\langle i|\mathbf{fr}|\varkappa E_z\rangle$ varies slowly in the scale of Δ. We then get for $W(\epsilon,F)$

$$W(\varepsilon,F)=w(\varepsilon,F)\exp\left(-\frac{2}{3F}(2(\Delta-\varepsilon))^{3/2}\right). \tag{7}$$

Here

$$w(\varepsilon,F)=\frac{F}{2\alpha_f}(1-\pi^{1/2}\xi e^{\xi^2}(1-\Phi(\xi)))^2,\quad \alpha_f^2=2(\Delta-\varepsilon).$$

At $\epsilon = 0$, formula (7) coincides exactly with the known expression for the rate of field-induced disintegration of an atomic negative ion,[21] and at $\epsilon \gg (\alpha F)^{1/2}$ it goes over into the corresponding expression of[9].

The summation over the vibrational quantum numbers, which is called for by the formulation of the problem, will be carried out assuming the equilibrium conditions

$$P_s=(1-\sigma_s)(\sigma_s)^{n_s^i},\ \sigma_s=e^{-\omega_s/T}.$$

The electronic factor depends only on the difference between the vibrational quantum numbers, so that the summation over $\{n_s^i\}$ is carried out in the usual manner (see, e.g.,[3]). We then obtain

$$\overline{W}(T,F)=\sum_{\{\nu_s\}}W(\varepsilon,F)\prod_s(\sigma_s)^{-\nu_s/2}\exp\left(-a_s\frac{1+\sigma_s}{1-\sigma_s}\right)I_{\nu_s}\left(2a_s\frac{\sqrt{\sigma_s}}{1-\sigma_s}\right),$$
$$\varepsilon=\Omega-\sum_s\omega_s\nu_s,\quad \nu_s=n_s^f-n_s^i. \tag{8}$$

Here $a_s = \frac{1}{2}\omega_s q_{0s}^2$ is the parameter of the electron-vibrational interaction in the sth mode (q_{0s} is the displacement of the equilibrium position along the sth normal coordinate), and $I_\nu(x)$ are Bessel functions of imaginary argument. The function $W(\epsilon,F)$ has no singularities at zero; we expand it in powers of $\Omega-\epsilon$ and introduce a differential operator with respect to an auxiliary parameter β:

$$\prod_s\Big(\sum_{s'}\omega_{s'}\nu_{s'}\Big)^k\exp\left(-\frac{\nu_s\omega_s}{2T}\right)=\left(\frac{\partial^k}{\partial\beta^k}\exp\Big(\beta\sum_s\omega_s\nu_s\Big)\right)_{\beta=1/2T} \tag{9}$$

We then have for $\overline{W}(T,F)$

$$\overline{W}(T,F)=\hat{W}\left(\frac{\partial}{\partial\beta},\frac{1}{2T}\right)$$
$$\times\sum_{\{\nu_s\}}\prod_s\exp[\beta\omega_s\nu_s-a_s(2n_s+1)]I_{\nu_s}[2a_s(n_s(n_s+1))^{1/2}]. \tag{10}$$

The operator $\hat{W}(\partial/\partial\beta,\frac{1}{2}T)$ is defined by the relation

$$\hat{W}\left(\frac{\partial}{\partial\beta},\frac{1}{2T}\right)f(\beta)=\left\{\sum_{k=0}^{\infty}\frac{W^{(k)}(0,F)}{k!}\frac{\partial^k}{\partial\beta^k}f(\beta)\right\}_{\beta=1/2T}, \tag{11}$$

where $W^{(k)}$ is the kth derivative of the function $W(\epsilon,F)$ with respect to $\Omega-\epsilon$. The most important function $W(\epsilon,F)$ is the dependence of the exponential factor. The corresponding terms of the expansion of the operator $\hat{W}(\partial/\partial\beta,\frac{1}{2}T)$ are proportional to the parameter $T(\Delta-\Omega)^{1/2}/F$, which is not small in general. On the other hand, if the operator $\partial/\partial\beta$ is taken into account in the function $w(\partial/\partial\beta,F)$, additional small terms $\sim T/\Delta$ appear. We therefore have, accurate to small terms proportional to the asymptotic parameter $F\Delta^{-3/2}$,

$$\hat{W}\left(\frac{\partial}{\partial\beta},\frac{1}{2T}\right)=w(\Omega,F)\left\{\exp\left[-\frac{2}{3}\tau_f\Delta_f\left(1+\frac{1}{\Delta_f}\frac{\partial}{\partial\beta}\right)^{3/2}\right](\ldots)\right\}_{\beta=1/2T},$$
$$\tau_f=2(2\Delta_f)^{1/2}/F,\quad \Delta_f=\Delta-\Omega. \tag{12}$$

We now interchange the order of the operations in (10) and use the known expression for the generator of the Bessel function. As a result we get

$$\overline{W}(T,F)=\hat{W}\left(\frac{\partial}{\partial\beta},\frac{1}{2T}\right)\exp\Big[-\sum_s a_s((2n_s+1)-2(n_s(n_s+1))^{1/2}\operatorname{ch}\beta\omega_s)\Big]. \tag{13}$$

As $a_s\to 0$, and $\overline{W}(T,F)\to W(\Omega,F)$, the condition

$$\sum_s a_s(n_s+1)^{1/2}\exp\left(\omega_s\left|\tau_f-\frac{1}{2T}\right|\right)\ll 1,$$

i.e.,

$$F\gg F_0\sim\omega\Delta_f^{1/2}\Big/\ln\sum_s a_s(n_s+1)^{1/2}, \tag{14}$$

determines in this manner the fields for which the electron-vibrational coupling is insignificant. An estimate of the intensity F_0 yields $F_0\sim 8\times 10^6$ V/cm($\omega = 0.1$ eV, $\Delta_f = 5$ eV), for the case of electron detachment from a molecule and $F_0\sim 10^6$ V/cm for an impurity center ($\omega = 0.04$ eV, $\Delta_f = 0.5$ eV).

3. ANALYSIS OF PARTICULAR CASES

Formula (13) is exact and provides in conjunction with (7) the solution of our problem in general form. Its practical applications are determined by the methods used to realize the differential operator (12), and these depend on the ratio of the characteristic energy parameters of the system and on the concrete form of the frequency dispersion function, or more accurately of the functions

$$\sum_s a_s\omega_s\exp(\pm\beta\omega_s).$$

We consider several examples, assuming $\Omega = 0$.

Let the electron-vibrational coupling be weak. Then, taking single-quantum absorption and emission into account, we obtain

$$\overline{W}(T,F)=w(\Omega,F)\exp\Big[-\sum_s a_s(2n_s+1)\Big]$$
$$\times\left\{\exp\left(-\frac{2}{3}\tau\Delta\right)+\sum_s a_s(n_s+1)\exp\left(-\frac{2}{3}\tau\Delta\left(1+\frac{\omega_s}{\Delta}\right)^{3/2}\right)\right.$$
$$\left.+\sum_s a_s n_s\exp\left(-\frac{2}{3}\tau\Delta\left(1-\frac{\omega_s}{\Delta}\right)^{3/2}\right)\right\}, \tag{15}$$
$$\tau=2(2\Delta)^{1/2}/F.$$

The first term determines the contribution of the elastic (relative to the vibrational subsystem) disintegration channel, while the second and third correspond to inelastic tunneling accompanied by production or absorption of one vibrational quantum. As expected, apart from the pre-exponential factor, the probability of field-induced disintegration of a localized state agrees with the known expression for single-phonon interband tunnel transitions.[16]

Formula (13) allows us to write down any term of the expansion of $\overline{W}(T,F)$ in terms of the electron-vibrational coupling, but in the general case the corresponding expressions are quite cumbersome. We neglect for simplicity the frequency dispersion, i.e., we consider a diatomic molecule or an "Einstein" crystal. We expand $\exp[a\cosh(\beta\omega)]$ in a series and perform all the operations called for by the operator $\hat{W}(\partial/\partial\beta, \frac{1}{2}T)$. We then obtain

$$\overline{W}(T,F)=\exp[-a(2n+1)]\sum_{s=0}^{\infty}\sum_{k=0}^{k=s}a^{s}\frac{(n+1)^{k}n^{k-s}}{k!(s-k)!}W(\Omega+\omega(s-2k),F). \tag{16}$$

The obtained series has a perfectly lucid physical meaning and corresponds to expansion of the function $\overline{W}(T,F)$ in terms of the number of phonon "production" and "absorption" acts. According to (16), the most probable decay channel is determined by the competition between four dimensionless factors: the electron-vibrational interaction constant a, the field-barrier penetrability $\exp[-\frac{2}{3}(2(\Delta_f-\omega(s-2k))^{3/2}]$, the relative probability $n/(n+1)$ of absorption of a quantum, and the statistical factor $(k!(s-k)!)^{-1}$.

We consider now low temperatures, when the main contribution in the sum over k is made by terms with $k=s$. Under these conditions the decay has a Poisson distribution that describes the successive acts of production of the vibrational quanta. Taking single-quantum absorption into account, and summing over all processes with emission, we obtain for $\overline{W}(T,F)$

$$\overline{W}(T,F)=w(\Omega,F)\exp[-{}^{2}/{}_{3}\tau\Delta+a(e^{-\tau\omega}-1)]\{1+an(T)e^{\tau\omega}\}. \tag{17}$$

The last term in (17) is a correction, i.e., the "low" temperature limit corresponds to the restriction

$$T\ll\omega/\ln ae^{\tau\omega}. \tag{18}$$

Formula (17) determines the rate of detachment of an electron in a sufficiently strong field and shows that at low temperatures the coupling of the electron with the vibrational subsystem always decreases the decay probability. If the frequency dispersion is appreciable, then it suffices to make in (17) the substitutions

$$ae^{-\tau\omega}\to\sum_{s}a_{s}e^{-\tau\omega_{s}},\quad ane^{-\tau\omega}\to\sum_{s}a_{s}n_{s}e^{\tau\omega_{s}}.$$

We consider now the case of sufficiently high temperatures and weak fields, when the decay is accompanied only by absorption of vibrational quanta. In this case, the contribution of the terms $k=0$ predominates in the expansion (16), and

$$\overline{W}(T,F)=e^{-a(2n+1)}\sum_{s=0}\frac{(an)^{s}}{s!}W(\omega s,F). \tag{19}$$

The decay follows then a Poisson distribution. In a weak field the number of absorbed quanta is high enough. This enables us to change from summation over s to integration and to use the saddle point method. As a result we get

$$\overline{W}(T,F)=\frac{w(\Omega,F)e^{\bar{\Omega}+1}}{(1+s_{0}\omega^{2}\tau^{2}/\bar{\tau}\bar{\Delta})^{1/2}}. \tag{20}$$

Here

$$\begin{gathered}\bar{\Omega}=-{}^{2}/{}_{3}\bar{\tau}\bar{\Delta}+ane^{\omega\bar{\tau}}(1-\omega\bar{\tau}/3)-a(2n+1),\\ \bar{\Delta}=\Delta-\Omega-s_{0}\omega,\quad\bar{\tau}=\tau[1-s_{0}\omega/(\Delta-\Omega)]^{1/2},\end{gathered} \tag{21}$$

s_0 is the most probable (average) number of absorbed quanta ($s_0=ane^{\omega\bar{\tau}}\gg1$) and is obtained from the equation

$$\ln\frac{s}{an}=\tau\omega\left(1-\frac{s\omega}{\Delta-\Omega}\right)^{1/2}. \tag{22}$$

According to (20)–(22), in a weak electric field the possibility of inelastic tunneling greatly increases the rate of electron detachment.

The case of high temperatures and of a strong field is easiest to investigate by using the general formula (13). We expand the operator $\hat{W}(\partial/\partial\beta, \frac{1}{2}T)$ in a series and apply it in the following manner:

$$\begin{aligned}&\hat{W}\left(\frac{\partial}{\partial\beta},\frac{1}{2T}\right)\prod_{s}\exp[-a_{s}(2n_{s}+1)+2a_{s}(n_{s}(n_{s}+1))^{1/2}\operatorname{ch}\beta\omega_{s}]\\ &\quad\approx\hat{W}\left(\frac{\partial}{\partial\beta},\frac{1}{2T}\right)\exp\Big[\sum_{s}a_{s}n_{s}\omega_{s}^{2}\beta^{2}\Big]\\ &\quad\approx\sum_{k=0}^{\infty}\frac{W^{(2k)}(0,T)}{k!}\frac{(\sum_{s}a_{s}n_{s}\omega_{s}^{2})^{k}}{\Delta^{2k}},\quad\sum_{s}a_{s}<1,\quad\Omega=0.\end{aligned} \tag{23}$$

It can be verified that (23) is exactly equivalent to averaging the electronic factor $W(\epsilon,F)$ over a Gaussian distribution:

$$\begin{gathered}\overline{W}(T,F)=\int d\varepsilon W(\varepsilon,F)e^{-\varepsilon^{2}/\Gamma^{2}},\\ \Gamma^{2}=4\sum_{s}a_{s}\omega_{s}^{2}n_{s},\quad n_{s}\gg1.\end{gathered} \tag{24}$$

The terms omitted in the derivation of (24) are of order of smallness $\tau\omega_s/n_s^3$, i.e., the quasiclassical approach to the calculation of $\overline{W}(T,F)$ is justified only under the condition

$$F\gg\Delta^{1/2}\omega/n^{3},\quad n\gg1. \tag{25}$$

Let us examine, finally, the limit of "quasielastic" tunneling, which corresponds to a low value of the energy exchanged by the electron with the vibrational subsystem. The average number $\bar{\nu}$ of the exchanged quanta can be shown to be the solution of the transcendental equation (we neglect for simplicity the frequency dispersion)

$$-\tau\omega\left(1+\frac{\omega\nu}{\Delta}\right)^{1/2}+\frac{\omega}{2T}+\frac{d}{d\nu}\ln I_{\nu}[a(n(n+1))^{1/2}]=0, \tag{26}$$

which has at $t=\frac{1}{2}T$, i.e., at

$$F=4T(2\Delta)^{1/2}, \tag{27}$$

a root $\nu=0$. Relation (27) determines the "critical field" for which processes with emission and absorption of phonons are equally probable. At $T<\omega$ the terms with phonon emission have practically no temperature dependence, whereas the terms with absorption depend on the temperature exponentially. It follows therefore that at a fixed F a strong temperature dependence takes place only under the condition $T > F/4\sqrt{\Delta}$. The available experimental data confirm well this conclusion of the theory (see, e.g., Fig. 4 of[11] and Fig. 6 of[15]).

Under conditions of quasielastic tunneling, the operator $\hat{W}(\partial/\partial\beta, \frac{1}{2}T)$ is realized in the following manner. We expand the exponential of the formula for $\hat{W}(\partial/\partial\beta, \frac{1}{2}T)$ in a series and apply the shift operator $e^{-\tau\partial/\partial\beta}$ in accord with the known rules. Then, accurate to quadratic terms of the argument of the exponential, we have for $\overline{W}(T,F)$

$$\overline{W}(T,F)=\frac{F}{2\alpha}\exp\left[-\frac{2}{3}\tau\Delta-\sum_s a_s(2n_s+1)\right]$$
$$\times\left\{\exp\left\{-\frac{\tau}{4\Delta}\frac{\partial^2}{\partial\beta^2}\right\}\prod_s \exp[2a_s(n_s(n_s+1))^{1/2}\operatorname{ch}\omega_s(\beta-\tau)]\right\}_{\beta=1/2T}. \tag{28}$$

The obtained expression permits a consistent account of the corrections to the quasielastic-tunneling rate, which is equal to

$$\overline{W}_0(T,F)=\frac{F}{2\alpha}\exp\left[-\frac{2}{3}\tau\Delta+2\sum_s a_s\operatorname{sh}\frac{\omega_s}{2}\left(\tau-\frac{1}{T}\right)\operatorname{sh}\frac{\omega_s}{2}\tau\operatorname{sh}^{-1}\frac{\omega_s}{2T}\right]. \tag{29}$$

The correction terms in (29) are of relative order of smallness $\delta\Delta^{-2}$, where δ is the variance of the energy distribution of the released electrons.

In concluding this section, let us examine the sufficient addition that can be introduced in (29) to take into account the interaction of the electron with a selected (local) oscillation with a nonequilibrium distribution over the levels. A concrete example may be the calculation of the autoionization width of a fixed electron-vibrational level $|i,n_0\rangle$ of an impurity-center molecule or an adsorbed atom. Expanding $W(\epsilon,F)$ in a series up to averaging over the equilibrium degrees of freedom, we obtain when account is taken of the higher-order terms

$$\overline{W}_{n_0}(T,F)=A_{n_0n_0}(t_1)\overline{W}_0(T,F). \tag{30}$$

Here

$$A_{n_0n_0}(t_1)=\langle n_0|G_f(t_1)|n_0\rangle \tag{31}$$

is the amplitude of the probability that the system will remain in the state $|n_0\rangle$ after two sudden changes of the inter action $U(R)$ with respect to a selected degree of freedom

$$U(R)=\begin{cases}U_i(R), & t<0, \quad t>t_1,\\ U_f(R), & 0<t<t_1,\end{cases}\qquad t_1=-i\tau.$$

In (31), $G_f(t_1)=(i\partial/\partial t-H_f(R))^{-1}$ is the time-dependent Green's function of the Schrödinger equation that describes the motion of the nuclear subsystem after the electron detachment. The actual form of the interaction $U_f(R)$ is immaterial here, and it can correspond, in particular to repulsion. (This takes place, for example, in field-induced desorption of atoms.) For the case of real durations t_1, the quantities $A_{n_0n_0}(t_1)$ were investigated earlier in[23]. For pure imaginary t_1, the analysis is similar. If we assume for $U_i(R)$ and $U_f(R)$ the model of a displaced oscillator and average $\overline{W}_{n_0}(T,F)$ over the equilibrium distribution, then (31) again leads to (29) with an additional term in the sum over s. It follows hence that in the quasielastic approximation the vibrational disintegration-rate factor is equal to the averaged probability amplitude for the absence of vibrational transition in a twofold sudden change of the interaction (at the instants of time $t=0$ and $t=t_1$) with respect to all normal coordinates of the system.

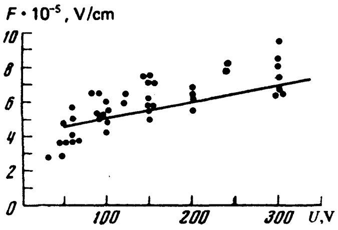

FIG. 1. Electric field intensity vs. the applied voltage (ZnS luminor). Points-summed data of [11-15], solid line—$F(U)$ plot assumed in the present paper.

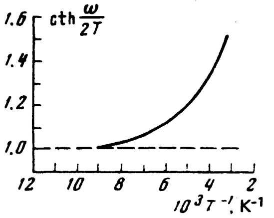

FIG. 2. Temperature dependence of $\ln\overline{W}(F,T)$ for ZnS (arbitrary units).

4. COMPARISON OF THEORY WITH EXPERIMENT

The processes of the destruction of the impurity centers of zinc sulfide by an electric field were systematically investigated recently by Kiveris and Pipinis.[11-15] Using mutually complementary procedures of measuring the electroluminescence flashes[11-15] and of the current pulse,[15] they determined, for different applied voltages U, the temperature dependence of the logarithm $\ln\overline{W}(T,F)$, of the electron detachment probability, and estimated (from the formulas of[13,16]) the corresponding fields. The theory expounded in Secs. 2 and 3 not only accounts for the experimental data,[11-15] but permits a more accurate reconstruction of the function $F(U)$ (see Fig. 1) and a determination of one of the main parameters of the impurity-center theory, namely the constant a.

The published data pertain in most cases to conditions of quasielastic tunneling and can be described by

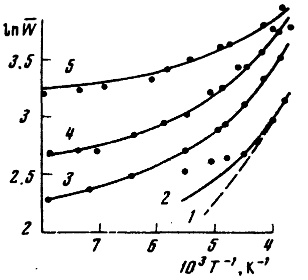

FIG. 3. Comparison of theory with experiment for ZnS: ($\Delta = 0.53$ eV, $\omega = 0.043$ eV, $m = 0.39m_e$). Points—experiment[15], solid lines—calculation by formula (32): curves 1 and 2—for $U = 60$ V, 3—$U = 90$ V, 4—$U = 150$ V, 5—$U = 300$ V. Dashed curve 1—calculation by formula (10) of[13].

TABLE I. Parameters of electron-vibrational interaction (doped ZnS:(A)).

A	Δ, eV	a eV	$\delta a/a$, %	Source of experimental data
Cu	0.42	0.37	15	[13]
	0.52	0.53	20	[13]
	0.53	0.30	25	[14]
	0.56	0.37	20	[13]
	0.60	0.25	40	[14]
	0.64	0.24	30	[13]
Ag	0.53	0.19	20	[14]
Pb	0.42	1.5	15	[12]

formula (29). In the ZnS crystal, the most significant is the interaction of the electron with the longitudinal optical phonons, whose dispersion can be neglected. Taking this into account we transform formula (29) and separate the temperature dependence of interest to us:

$$\ln \overline{W}(T,F)=\text{const}+d\,\text{cth}\frac{\omega}{2T},\quad d=2a\,\text{sh}^2\frac{\omega\tau}{2}. \qquad (32)$$

Figure 2 shows the function $f(T)-\coth(\omega/2T)$ for $\omega=0.043$ eV (this corresponds to the energy of the LO phonon of the ZnS lattice). Even a simple comparison of Fig. 2 with experiment (see Fig. 3) shows that when the parameter d is suitably chosen the curves can be made congruent. The remainder of the calculation reduces to the choice of a single function $F(U)$ for all the experiments (the solid line in Fig. 3) and reconstruction of the parameters a, which depend on the individual properties of the impurity centers. The accuracy with which the field is reconstructed in this case is higher the lower the voltage. At $U=50$ V and $\Delta=0.4$ eV, for example, a 10% variation of F changes $\ln\overline{W}(T,F)$ by one order of magnitude. The degree of reliability of the entire calculation is monitored by the relative error in the reconstruction of the parameter $\underline{a}$ from the experimental $\ln\overline{W}(T,F)$ curves plotted at different U. The results of the calculations are illustrated in Figs. 1–3 and are also listed in the table.

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[1] More accurate conditions, that include the temperature and the electron-vibrational interaction constant, are given below.

[2] All the calculations are analogous for functions of the form $A\gamma^n e^{-\alpha r}$.

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Translated by J. G. Adashko