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Capture of Conduction Electrons by Charged Defects in Ionic Crystals

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Capture of conduction electrons by charged defects of an ionic crystal lattice is regarded as a one-quantum thermal transition from the continuous spectrum to an excited state of the discrete spectrum. The role of the perturbation is played by the nonconfigurational interaction which in an ideal crystal leads to ordinary polaron scattering. The capture probability as a function of polaron velocity has been computed and the temperature dependence of current-carrier lifetime has been established.

1. INTRODUCTION

IN the phenomenological theory of semiconductors, the recombination coefficients of conduction electrons with "impurity centers" such as ion vacancies or excess interstitial ions are usually regarded as parameters to be determined by comparing the theory with experiment. The large number of such parameters endows the formulas of the phenomenological theory with excessive approximational flexibility so that the comparison of the theory with experiment is sometimes inconclusive. Therefore, calculation of the probability of electron capture by an impurity center using the methods of a microscopic theory is of considerable interest.

We shall not in this article attempt a complete review of the theoretical work on this problem. We shall, however, indicate that a treatment of the problem very similar to ours was first published by Adirovich,¹ who regarded electron capture as a quantum transition induced by the nonconfigurational interaction of an electron with ion motions (the violation of adiabaticity). Adirovich's proposed model of a pulsating double layer enabled him to make a qualitative estimate of capture probability.

A theoretical formula for the recombination coefficient which does not contain undetermined parameters and which permits comparison of the theory with experiment was obtained by Pekar,² who divided the process of electron capture by an impurity center into the diffusion of an electron to a lattice defect and direct thermal transition to a discrete energy level. In crystals where conduction electron mobility is low, the first part of the process can play the deciding role.

Pekar and the present author³ made a comparison of the recombination coefficient calculated on this hypothesis with experimental data on electron capture by *F* centers in alkali halide crystals and obtained satisfactory results. Nevertheless, without a quantum mechanical calculation of the thermal transition probability (of an electron) to a discrete level, the "diffusion" theory of recombinations is of uncertain applicability. There are undoubtedly cases in which the second stage of the process rather than the first, plays the deciding role.

The present article attempts a quantum mechanical calculation of the probability for electron capture by a positively charged ionic crystal lattice defect (such as a negative ion vacancy). Such a

process occurs in connection with the coloring of ionic crystals by x-rays. The captured electrons form F centers.

In a number of recently published investigations of the theory of thermal ionization of F centers (see, for example, the articles by O'Rourke and by Vasileff⁴), the wave functions of the continuous spectrum are given in the form of the product

$$\chi(\mathbf{r}) \prod_x \Phi_n(q_x)$$

of the purely electronic function and the wave functions Φ_{n_k} of undisturbed normal lattice oscillators. These articles thus ignore the effect of inertial polarization of the ionic crystal on the electron states of the continuous spectrum as well as the shift of the equilibrium positions of the phonon field oscillators which results from interactions with electrons. Such an approximation is unacceptable since at large distances from a defect, a conduction electron forms a polaron and its state is described by the damped wave function

$$\psi(\mathbf{r} - \xi),$$

belonging to the discrete spectrum, where ξ is the translational radius vector of the polaron which characterizes the location of the center of symmetry of the polarized potential well.

Confining ourselves to strong coupling between an electron and the longitudinal phonon field we shall use as a basis the Hamiltonian of Pekar's theory of polarons:

$$\hat{H} = -(\hbar^2/2\mu)\Delta + V(\mathbf{r}) + \sum_x A_x(\mathbf{r})q_x + 1/2\hbar\omega \sum_x (q_x^2 - \partial^2/\partial q_x^2). \quad (1.1)$$

Here μ is the effective electron mass in the conduction band, $V(\mathbf{r})$ is the interaction potential between an electron and a lattice defect, q_k are the normal coordinates of the phonon field, ω is the frequency limit of longitudinal optical oscillations (whose small dispersion we neglect);

$$A_x(\mathbf{r}) = -\frac{e}{x} \sqrt{\frac{c\hbar\omega}{4\pi}} \int \frac{(x, \text{grad } \chi_x(\mathbf{r}')) d\tau'}{|\mathbf{r} - \mathbf{r}'|}, \quad (1.2)$$

where $c = 1/n^2 - 1/\epsilon$ is the inertial polarization constant of the crystal. The functions

$$\chi_x(\mathbf{r}) = \sqrt{\frac{2}{L^3}} \begin{cases} \cos(x\mathbf{r}) & \text{for } x_x \geq 0, \\ \sin(x\mathbf{r}) & \text{for } x_x < 0 \end{cases} \quad (1.3)$$

form a complete orthonormal set in the space L^3 .

Keeping in mind that a weakly coupled electron is a fast subsystem while the lattice oscillators comprise a slow subsystem, we can employ an adiabatic method, that is, we can obtain an approximate eigenfunction of the operator (1.1) as the product

$$\Psi(\mathbf{r}, \dots, q_x, \dots) = \psi(\mathbf{r}, \dots, q_x, \dots) \Phi(\dots, q_x, \dots), \quad (1.4)$$

where the electronic function satisfies the equation

$$\left[-(\hbar^2/2\mu)\Delta + V(\mathbf{r}) + \sum_x A_x(\mathbf{r})q_x \right] \psi(\mathbf{r}, q) = E(q)\psi(\mathbf{r}, q), \quad (1.5)$$

and the eigenvalues of

$$\left[E(q) + 1/2\hbar\omega \sum_x (q_x^2 - \partial^2/\partial q_x^2) \right] \Phi = H\Phi \quad (1.6)$$

are approximate values of the energy of the entire system. In deriving (1.6) we omitted terms resulting from the action of the kinetic energy operator of the slow subsystem on the electronic function ("nonadiabatic" terms).

In our case of strongly excited states the electron moves in a quasi-classical orbit of large radius. In this case, the field of the defect affects the electronic wave function less than the polaron effect in a perfect crystal. This means that the center of localization of the function ψ will not coincide with the center of the defect Coulomb field (the coordinate origin) and we are justified in setting

$$\psi(\mathbf{r}, \dots, q_x, \dots) = \psi_0(\mathbf{r} - \xi, \dots, q_x, \dots). \quad (1.7)$$

Following the traditional method, we can calculate ψ_0 on the assumption that the potential energy of the slow subsystem differs little from its equilibrium (minimum) value in the configuration

$$(q_x)_{\min} = q_{x\xi} = -A_{x\xi}/\hbar\omega, \quad (1.8)$$

where

$$A_{x\xi} = \int A_x(\mathbf{r}) |\psi_0(\mathbf{r} - \xi)|^2 d\tau. \quad (1.9)$$

If we limit ourselves to a first-order perturbation

calculation of $E(q)$ from (1.5), then (1.6) becomes

$$\left\{ I[\psi_0] + W(\xi) + \frac{1}{2}\hbar\omega \right. \quad (1.10)$$

$$\left. \times \sum_x [(q_x - q_{x\xi})^2 - \partial^2 / \partial q_x^2] \right\} \Phi = H\Phi;$$

$$I[\psi_0] = (\hbar^2 / 2\mu) \int |\nabla\psi_0|^2 d\tau - \frac{1}{2}\hbar\omega \sum_x q_{x\xi}^2 \quad (1.11)$$

is independent of ξ and

$$W(\xi) = \int V(\mathbf{r}) |\psi_0(\mathbf{r} - \xi)|^2 d\tau. \quad (1.12)$$

Proceeding to an examination of the final form of ψ_0 , we note that in the limiting case $\xi \rightarrow \infty$ this function describes the state of the electron in a polaron. However the field of the defect destroys the spherical symmetry of ψ_0 and the radius of the electronic state is changed. The first of these effects can be regarded as the polarization of the electronic "cloud" in the polaron by the Coulomb field of the defect. The author's method of calculating the polarizability of an F center⁵ enables us to show that when

$$\xi > 6.19 / \alpha \sqrt{\varepsilon C} = 1.24 r_p / \sqrt{\varepsilon C}, \quad (1.13)$$

where

$$\alpha = \mu e^2 c / 2\hbar^2,$$

and

$$r_p = 5/\alpha$$

is the so-called polarization radius of the polaron, the deformation of ψ_0 can be neglected.

In Ref. 6 it was shown that when

$$\xi > 5/\alpha = r_p, \quad (1.14)$$

which practically coincides with (1.13), it is also possible to neglect the change of radius of the electronic state in the polaron. Assuming that (1.13) and (1.14) are satisfied at all points of the quasi-classical orbits of strongly excited states we can therefore take ψ_0 in the form of the usual electronic wave function in a polaron²:

$$\psi_0(r) = \sqrt{\alpha^3 / 7\pi} (1 + \alpha r) e^{-\alpha r}. \quad (1.15)$$

We note, finally, that according to Ref. 6, for a Coulomb impurity center subject to condition (1.14), W is approximated with sufficient accuracy by a Coulomb potential.

The eigenfunction of (1.10) will be sought in the form

$$\text{equation } \Phi(\xi, \dots, q'_x \dots),$$

where

$$q'_x = q_x - q_{x\xi}, \quad (1.16)$$

and ξ is a function of the variables q_k . The choice of this function is to some extent arbitrary. According to Pekar², the dependence of ξ on q_k is given implicitly by

$$\sum_x q_x \partial q_{x\xi} / \partial \xi_i = 0 \quad (i = 1, 2, 3). \quad (1.17)$$

The insertion of

$$\Phi(\xi, q'_x)$$

after transformations which are entirely analogous to the corresponding transformations in polaron theory changes (1.10) to the form

$$\left\{ I[\psi_0] + W(\xi) - (\hbar^2 / 2M) \Delta_\xi \right. \quad (1.18)$$

$$\left. + \frac{1}{2} \sum_x \hbar\omega (q'_x)^2 - \partial^2 / \partial q_x'^2 \right\}$$

$$(q_x)_{\min} = q_{x\xi} = -A_{x\xi} / \hbar\omega,$$

where M is the effective mass of the polaron,

$$\hat{H}' = (\hbar^2 / 2M) \sum_x \Delta_\xi q_{x\xi} \partial / \partial q'_x; \quad (1.19)$$

$$\hat{H}'' = (\hbar^2 / 2M) \quad (1.20)$$

$$\times \sum_x \sum_\lambda (\nabla_\xi q_{x\xi}, \nabla_\xi q_{\lambda\xi}) \partial^2 / \partial q'_x \partial q'_\lambda.$$

Equation (1.18) differs from the analogous equation of the polaron theory not only because of the presence of the term $W(\xi)$ but also in that the number of variables including the vector ξ exceeds by 3 the number of degrees of freedom of the lattice. Therefore, (1.18) must in general be interpreted along with the supplementary relations (1.17).

However, it is possible to consider the more general problem described by (1.18), where ξ and

q'_k are independent variables. Insertion of the dependence of ξ on q'_k into the solution of this general problem leads to a solution of our special problem. This substitution can be performed in the last stage of the calculations, thus including, in particular, the entire perturbation theory in the generalized stage. Therefore the transition matrix elements can be calculated from the zero-order approximation eigenfunctions of the generalized equation (1.18).

The zero-order approximation generalized functions are obtained from (1.18) if the operators \hat{H}' and \hat{H}'' , which in the polaron theory lead to one-quantum and two-quantum scattering, respectively, are regarded as small perturbations. When these operators are omitted, the variables in (1.18) are separable and the eigenfunctions and energies of the zero-order stationary states are:

$$\Phi_{n,n_x}^0(\xi, \dots, q'_x, \dots) = \varphi_n(\xi) \prod_x \Phi_{n_x}(q'_x), \quad (1.21)$$

$$H_{n,n_x}^0 = I[\psi_0] + E_n + \hbar\omega \sum_x (n_x + 1/2). \quad (1.22)$$

Here φ_n and E_n satisfy the Schrödinger equation

$$-(\hbar^2/2M)\Delta_\xi \varphi_n + W(\xi)\varphi_n = E_n \varphi_n, \quad (1.23)$$

which describes the motion of a quasi-particle (polaron) in a Coulomb field. The Φ_{nk} are the wave functions of the harmonic oscillators. The criterion for the applicability of our approximation to strongly excited discrete F -center levels can be derived from the virial theorem and the inequality (1.14):

$$n^2 > 10ZM/\varepsilon c\mu, \quad (1.24)$$

where n is the principal quantum number of the hydrogen-like term.

In the present article we confine ourselves to an examination of one-quantum transitions between zero-order stationary states resulting from the perturbation \hat{H}' . It is assumed that the initial polaron state belongs to the continuous spectrum and that its energy is given by

$$E_n = E(\mathbf{k}) = \hbar^2 k^2 / 2M \leq \hbar\omega. \quad (1.25)$$

Then a transition with emission of a phonon takes place to one of the discrete states, and therefore

represents the localization of the conduction electron close to the impurity center. This transition will be regarded as electron capture.

The captured electron can subsequently be ejected into the continuous spectrum again by absorption of a phonon, but there is a much greater probability (when the temperature is not high) that it will "drop" to the ground state of the F -center in a thermal or optical transition. Thermal transitions between discrete levels were investigated by Huang and Rhys.⁷

The single-phonon capture proposed here is, of course, not the only possible mechanism. A possible competing mechanism is a "multi-phonon" transition associated with deformation of the electronic wave function ψ by the field of the impurity center. As a result of this deformation, the equilibrium values of the normal coordinates q_k of the phonon field differ in the various electronic states, and the corresponding oscillator wave functions

$$\Phi_{n_x}(q_x - q_{x\xi})$$

and

$$\Phi_{n'_x}(q_x - q_{x\xi'})$$

become nonorthogonal. A probability of a multi-phonon transition exists in the first perturbation approximation. We intend to investigate such transitions in one of our future articles.

2. MATRIX ELEMENT OF A SINGLE PHONON TRANSITION

For the succeeding calculations we introduce the unit of length

$$a_0 = \varepsilon \hbar^2 / Me^2. \quad (2.1)$$

In the formulas which follow all quantities having the dimension of a length or a reciprocal length will be expressed in units of a_0 and a_0^{-1} , respectively.

If we neglect the small dispersion of the longitudinal optical vibrations of the crystal and use Pekar's expressions² for M and $q_k \xi$ the perturbation operator becomes

$$\hat{H}' = -\frac{V\pi}{100} \hbar\omega (\varepsilon c)^{1/2} \left(\frac{A}{\hbar\omega}\right)^{1/2} \quad (2.2)$$

$$\times \sum_x \frac{x(1+x^2/28x^2)}{(1+x^2/4x^2)^2} \chi_x(\xi) \partial / \partial q'_x,$$

where all of Pekar's notation² has been retained. In particular

$$A = \mu e^4 / 2\hbar^2 \varepsilon^2, \quad (2.3)$$

$$\alpha = 21.6 (\varepsilon c)^{-3} (\hbar\omega / A)^2. \quad (2.4)$$

The transition between stationary states

$$k, \dots, n_x, \dots \rightarrow n, \dots, n_x', \dots$$

corresponds to the matrix element

$$\begin{aligned} & (k, \dots, n_x, \dots | \hat{H}' | n, \dots, n_x', \dots) \\ &= \int \varphi_k^*(\xi) \prod_x \Phi_{n_x}(q'_x) \hat{H}' \varphi_n(\xi) \prod_x \Phi_{n'_x}(q'_x) dq'_x d\xi. \end{aligned} \quad (2.5)$$

For the quantum transition with emission of a phonon $\hbar\omega_x$, integration over the variables q'_x gives

$$\prod_x \int \dots dq'_x = \sqrt{(n_x + 1)/2} \quad (2.6)$$

for an allowed transition; one term of the sum in (2.2) remains, corresponding to the emitted phonon $\hbar\omega_x$.

In proceeding to integrate over the variables ξ we make the following simplifying assumptions:

1) We limit ourselves to a consideration of a transition between *s*-states of the Coulomb field, setting

$$\varphi_n(\xi) = R_n(\xi) / 4\pi, \quad (2.7)$$

where $R_n(\xi)$ is the radial function

2) We consider a transition to a strongly excited state of the discrete spectrum with a principal quantum number which satisfies the inequality

$$n^2 > 10M / \varepsilon c \mu \gg 1. \quad (2.8)$$

In this state the most probable value of ξ for the polaron is $\sim n^2 \gg 1$ and, consequently, the principal role in the Laguerre polynomial is played by a higher term. Consequently, we shall use the following approximate radial function for the discrete spectrum:

$$R_n(\xi) \cong (2/n)^{n+1} \xi^{n-1} e^{-\xi/n} / \sqrt{(2n)!}. \quad (2.9)$$

3) The wave function of the continuous spectrum will be replaced by its asymptotic expression, which is valid for large ξ :

$$R_k(\xi) \cong \sqrt{2/L} \xi^{-1} \sin(k\xi + \ln(2k\xi)/k + \delta), \quad (2.10)$$

$$\delta = \arg \Gamma(1 - i/k). \quad (2.11)$$

The wave function $R_k(\xi)$ is normalized in a sphere of radius $L \rightarrow \infty$:

4) We assume $Z = 1$. For $Z \neq 1$ ϵ in the final result can be replaced by ϵ/Z .

Using the wave functions (2.9) and (2.10), we obtain after some calculation:

$$\begin{aligned} & (k, n_x | \hat{H}' | n, n_x + 1) \\ &= 7.06 \cdot 10^{-3} \sqrt{2\pi} L^{-2} \hbar\omega_x (\varepsilon c)^{1/2} \\ & \times \left(\frac{A}{\hbar\omega}\right)^{1/2} \sqrt{n_x + 1} \frac{(1 + \alpha^2/28\alpha^2) 2^n |\Gamma(n + i, k)|}{(1 + \alpha^2/4\alpha^2)^4 n^{n+1/2} V(2n)!} \end{aligned} \quad (2.12)$$

$$\times \operatorname{Re}\{f(-x) - f(x)\} e^{i(\gamma + \ln(2k)/\hbar)},$$

where

$$x_x \geq 0 \text{ and } f(x) \quad (2.13)$$

$$= [1/n - i(k - x)]^{-(n+i/k)}, \quad \gamma = \sum_{t=1}^{n-1} \arg(t + i/k).$$

The dimensionless parameters k and n in (2.12) are related to each other under energy conservation by

$$\hbar^2 k^2 / 2Ma_0^2 = -Me^4 / 2\hbar^2 \varepsilon^2 n^2 + \hbar\omega_x \quad (2.14)$$

or

$$k^2 + 1/n^2 = p^2, \quad (2.14a)$$

$$p = 6.56 (\varepsilon c)^{-2} (\hbar\omega/A)^{1/2} \ll 1$$

for the majority of ionic crystals.

From (2.14) and (2.14a) it follows that capture is possible only for small values of the dimensionless wave number k . This enables us to introduce an approximate formula for γ , with the sum in (2.13) replaced by an integral:

$$\gamma = \sum_{t=1}^{n-1} \operatorname{arc} \operatorname{ctg} kt \quad (2.15)$$

$$\cong (n-1) \operatorname{arc} \operatorname{ctg} k(n-1) + \frac{1}{2k} \ln [1 + k^2(n-1)^2].$$

3. THE PROBABILITY OF ELECTRON CAPTURE BY A DEFECT

The probability per unit time of a transition from a state of the continuous spectrum to a discrete level can be calculated from the familiar formula

$$\omega_{\kappa}(k) = (2\pi/\hbar)\rho(E)|\langle k, n_{\kappa} | H' | n, n_{\kappa} + 1 \rangle|^2, \quad (3.1)$$

where $\rho(E)$ is the density of states in the energy range of the continuous spectrum. For the wave functions of the continuous spectrum which we have normalized in a sphere of radius L

$$\rho(E) = (L/2\pi)(43.1/Ak)(\varepsilon c)^{-4}(\hbar\omega/A)^2. \quad (3.2)$$

The expression for the transition probability which is obtained after inserting (2.12) and (3.2) in (3.1) contains the wave number κ of the emitted phonon. When account is taken of the dispersion law of optical vibrations, this quantity is determined with complete accuracy from energy conservation. If, however, we neglect dispersion and replace all longitudinal optical frequencies by the frequency limit ω , the magnitude of κ becomes indeterminate. In order to eliminate this uncertainty, the expression obtained for the probability can be averaged over all values of κ by the formula

$$\bar{\omega}(k) = \frac{1}{z} \int \omega_{\kappa}(k) dz(\kappa), \quad (3.3)$$

$$dz(\kappa) = L^3 \kappa^2 d\kappa / 2\pi^2,$$

where $dz(\kappa)$ is the number of normal frequencies in the interval $d\kappa$ and $z = L^3/\Omega$, where Ω is the volume of a unit crystal cell, is the total number of normal frequencies in the fundamental region.

The probability (3.3) must furthermore be multiplied by the total number NL^3 of defects in the fundamental crystal region. The probability of electron capture then becomes

$$\omega(k) = 1.07 \cdot 10^{-3} N \Omega (\varepsilon c)^9 \omega \left(\frac{A}{\hbar\omega} \right)^6 \quad (3.4)$$

$$\times \frac{2^{2n} |\Gamma(n+i/k)|^2}{\pi k n^{2n+1} (2n)!} \\ \times (\bar{n}_{\kappa} + 1) \int_0^{\infty} R_h^2(\kappa) \frac{\kappa^2 (1 + \kappa^2/28\alpha^2)^2 d\kappa}{(1 + \kappa^2/4\alpha^2)^8}.$$

In deriving this last formula, n_k was taken outside of the summation over κ (integration in κ space) and given its average equilibrium value

$$\bar{n}_{\kappa} = (e^{\hbar\omega/\Theta} - 1)^{-1}, \quad (3.5)$$

where Θ is the statistical temperature.

In accordance with (2.2)

$$R_k(\kappa) = \text{Re} \{ f(-\kappa) - f(\kappa) \} e^{i(\gamma + \ln(2k)/k)}. \quad (3.6)$$

We have not been able to calculate the complicated integral in (3.4) in finite form. However, approximate values of the integral can be obtained by investigating the integrand.

It is easily seen that the function

$$f(\kappa)^2 = (1 + y^2)^{-n} n^{2n} e^{-(2/h) \text{arc tg } y}, \quad (3.7)$$

$$y = n(k - \kappa)$$

has the character of a δ function with its maximum at

$$y = y_m = -1/nk; \quad \kappa_m = p^2/k. \quad (3.8)$$

The maximum of $|f(-\kappa)|$ lies in the region of negative κ , i.e., outside the limits of integration in (3.4), and the greatest value of this function in the integration interval (for $\kappa = 0$) is many orders smaller than the maximum of $|f(\kappa)|$. On this basis we set

$$R_k(\kappa) \cong \text{Re} e^{i(\gamma + \ln(2k)/k)} f(\kappa) \quad (3.9)$$

$$= (1 + y^2)^{-n/2} n^n e^{-(1/k) \text{arc tg } y} \cos \vartheta_{\kappa},$$

$$\vartheta_{\kappa} = \gamma + \ln(2k)/k \quad (3.10)$$

$$- \ln(1 + y^2)/2k + n \text{arc tg } y.$$

The other factor of the integrand in (3.4) is

$$f_1(\kappa) = \kappa^2 (1 + \kappa^2/28\alpha^2)^2 (1 + \kappa^2/4\alpha^2)^{-8}, \quad (3.11)$$

which is also expressed by a curve with its peak at $\kappa = \kappa_1 \approx 0.8\alpha$. However, by comparison with (3.7) this function changes very smoothly.

Let us consider the two limiting cases.

a) The case of relatively fast electrons, when

$$k \sim p; kn \gg 1. \quad (3.12)$$

In this case $\kappa_m \sim p$ and since as usual in ionic crystals $p \gg a$ the main part of the δ curve (3.7) corresponds to the region of smooth decrease of $f_1(\kappa)$. Therefore $f_1(\kappa)$ can be taken outside the integral sign in (3.4) using $\kappa = \kappa_m = p^2/k$. We note, furthermore, that as a result of (3.8) $|y| \ll 1$ in the vicinity of the maximum of (3.7), so that, in accordance with (3.10),

$$\vartheta_\kappa \approx \vartheta_m + ny.$$

This indicates that $\cos^2 \vartheta_\kappa$ oscillates extremely rapidly in the indicated region ($n \rightarrow \infty!$) and can be taken outside the integral sign with an average value of $1/2$. Thus, in the limiting case under consideration,

$$\int_0^\infty R_k^2(z) f_1(x) dz \quad (3.13)$$

$$\approx (p^4/2k^2) (1 + p^4/28\alpha^2 k^2)^2 (1 + p^4/4\alpha^2 k^2)^{-8}$$

$$\times n^{2n} \int_{-\infty}^{nh} (1 + y^2)^{-n} \cdot e^{-(2/k) \arctg y} dy.$$

The integral in (3.13) with the substitution $y = \tan z$ reduces to

$$I(n, k) = \int_{-\pi/2}^{z_0} e^{-2z/k} \cos^{2(n-1)} z dz,$$

where $z_0 = \arctan nk \sim \pi/2$ can be replaced by infinity because of the rapid decrease of the integrand. In this case $I(n, k)$ reduces to the tabulated integral⁹

$$I(n, k) \approx e^{\pi/k} \int_0^\infty e^{-2x/k} \sin^{2(n-1)} x dx \quad (3.14)$$

$$= ke^{\pi/k} (2n-2)! |\Gamma(1+i/k)|^2 / 2^{2n-1} |\Gamma(n+i/k)|^2.$$

By using the well-known properties of the Γ function we easily obtain

$$k! |\Gamma(1+i/k)|^2 = \pi / \text{sh}(\pi/k) \approx (2\pi/k) e^{-\pi/k},$$

since $k \ll 1$. Collecting the results we arrive in this limiting case at the formula

$$\omega(k) = N\Omega k \omega \varepsilon c (\bar{n}_\kappa + 1) \quad (3.15)$$

$$\times \left(\frac{p^2}{k^2} - 1 \right)^2 \frac{(1 + p^4/28\alpha^2 k^2)^2}{(1 + p^4/4\alpha^2 k^2)^8}.$$

b) The case of slow electrons, when

$$k \ll p; n \sim 1/p. \quad (3.16)$$

In this case, $\kappa_m \gg \kappa_1$ and the maximum of the δ function (3.7) is located in the region where $f_1(\kappa)$ decreases rapidly to zero. A numerical tabulation shows that in this case the most important region of the integral in (3.4) is nevertheless the "half width" of the δ curve since in this region $f_1(\kappa)$ is approximated very closely by

$$f_1(\kappa) \approx (2\alpha)^{12} n^{10} / 49 (1 + y^2)^5. \quad (3.17)$$

When $\cos^2 \vartheta_\kappa$ is replaced by its average value, just as in case a), we can obtain

$$\omega(k) = \frac{4.45 \cdot 10^{16} N \Omega \omega}{2\pi k (\varepsilon c)^{27}} \left(\frac{\hbar \omega}{A} \right)^{18} (\bar{n}_\kappa + 1) \quad (3.18)$$

$$\times \frac{2^{2n} |\Gamma(n+i/k)|^2 n^8}{(2n)!} I(n+5, k).$$

The insertion of $I(n+5, k)$ from (3.14) leads in the considered case of slow-electron capture to

$$\omega(k) = 1.97 \cdot 10^8 N \Omega \omega (\varepsilon c)^{-7} (\hbar \omega / A)^3 \quad (3.19)$$

$$\times (\bar{n}_\kappa + 1) L(n) k^3 (p^2/k^2 - 1)^{-3},$$

$$L(n) = \prod_{i=1}^8 (1 + i/2n) \sim 1. \quad (3.20)$$

As a numerical example we took a KCl crystal, for which $\varepsilon c = 1.2$; $A = 1.10$ eV; $\hbar \omega = 0.026$ eV and $p = 0.0166$. Figure 1 shows the dependence of the probability for single-phonon capture on polaron velocity (wave number). The curve was plotted for "large" and small k according to (3.15) and (3.19) and was extrapolated graphically into the region of intermediate values of κ . We note that the peak of the curve lies in the region of "large" k to which (3.15) applies.

4. TEMPERATURE DEPENDENCE OF CAPTURE PROBABILITY

The temperature dependence of capture probability can be obtained by statistical averaging of

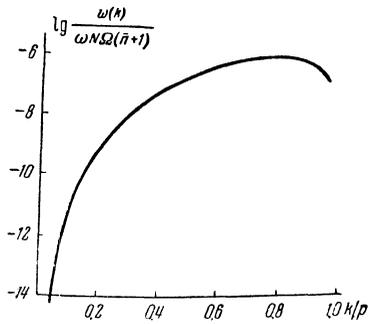


Fig. 1

the foregoing expressions. We assume that free polarons are in thermal equilibrium with the lattice. The Maxwellian distribution of the polarons is

$$F(k) dk = 4p^{-3} \sqrt{\beta^3/\pi} e^{-\beta k^2/p^2} k^2 dk, \quad (4.1)$$

where $F(k)$ is the distribution function over the wave numbers and $\omega = \bar{n} \omega / \Theta$. The statistically averaged probability is

$$\bar{\omega} = 4 \sqrt{\beta^3/\pi} \int_0^1 \omega(p\xi) e^{-\beta \xi^2/p^2} d\xi, \quad \xi = k/p. \quad (4.2)$$

We were not able to calculate $\bar{\omega}$ from (4.2) in general form. We therefore confined ourselves to tabulating the dependence of $\bar{\omega}$ on β for a KCl crystal by numerical integration. The results of the calculations are shown in Fig. 2. The capture probability is extremely small at low temperatures but increases rapidly with heating and reaches its peak at $T \sim 120^\circ \text{K}$. With further heating the

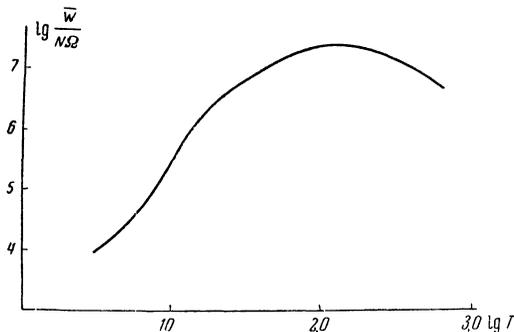


Fig. 2

probability decreases relatively slowly (by a factor of about 4 between 120° and 600°K).

The minimum lifetime of polarons in a KCl crystal ($\Omega \approx 6.2 \cdot 10^{-23} \text{ cm}^3$) with reference to one-quantum capture is

$$\tau_{\min} \sim 5 \cdot 10^{14} N^{-1} \text{ sec.} \quad (4.3)$$

In Pekar's diffusion theory the polaron lifetime against capture by Coulomb centers is calculated from the formula²

$$\tau = \varepsilon / 4\pi e u N, \quad (4.4)$$

where u is the polaron mobility, which according to Ref. 2 is given by the relation $u = u_0 (e^\beta - 1)$

For KCl $u_0 = 463$ abs. units. For $T = 122^\circ \text{K}$ ($\beta = 2.5$) formula (4.4) gives $\tau \sim 1.5 \cdot 10^5 N^{-1}$ sec. Comparison with (4.3) shows that, in the case considered polaron diffusion to lattice defects is not a "bottleneck" in the recombination process. The diffusion theory will hardly be applicable at very low temperatures also. We emphasize that our conclusion does not refer to capture by neutral centers when, as was noted above, the diffusion theory leads to satisfactory agreement with experiment.

We propose in the future to make a comparison of the theory with experimental findings, especially with reference to the kinetics of the thermal bleaching of colored crystals. At the present stage of our investigation such a comparison would be premature since, in addition to what has been presented above, we require a theoretical calculation for multi-phonon capture and thermal ionization of F -centers. Subsequent articles will be devoted to these calculations.

In conclusion the author wishes to acknowledge his indebtedness to Professor S. I. Pekar, who made a number of very valuable comments.

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