

IMPURITY LIGHT ABSORPTION FOR ARBITRARY ELECTRON-PHONON COUPLING

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The spectral admittance of an impurity-phonon system in a spatially uniform high-frequency electric field is calculated using the method of continual path integration. In the zeroth approximation the system is described by a trial Lagrangian in which both the Coulomb and the electron-phonon interactions are imitated by elastic forces. The intensity of the no-phonon and one-phonon impurity-absorption peaks is derived (in a first approximation) for shallow hydrogen-like traps in ionic crystals. The obtained formulae are valid in the case of small heat release and arbitrary electron-phonon coupling. The temperature shift of the impurity absorption lines is also calculated.

THE theory of light absorption by local centers in semiconductors and insulators departs usually from an adiabatic approximation, in which the localized electron acts as a fast subsystem with respect to the lattice vibrations^[1-4]. However, the adiabatic approximation loses accuracy when the Bohr frequency of the pure electronic transition and the frequencies of the impurity-active phonons have the same order of magnitude. Such a situation arises on investigation of shallow traps of the F-center type in ionic crystals having a polaron binding constant $\alpha \approx 1$. To calculate the energy spectrum of such centers one uses variational methods which are not connected with the adiabatic approximation or perturbation theory^[5-7].

A method of arbitrary coupling was developed earlier^[7] for the calculation of the thermodynamic functions of the impurity-phonon system. This method is extended in the present work to the theory of impurity light absorption. The calculation is performed with the technique of the nonequilibrium density matrix and the use of the Lagrangian formalism. The last was developed in the work of Feynman et al.^[8] on polaron mobility, and of Feynman and Vernon^[9] on fluctuation theory in interacting quantum systems.

1. THE DENSITY MATRIX OF A LOCALIZED ELECTRON

In the impurity absorption region we may neglect the fundamental absorption of the ideal crystal. Keeping the terms of the first order with respect to the concentration N of local centers, we easily obtain for the absorption coefficient the

formula

$$\kappa(\nu) = \frac{2\pi N e^2}{c_0 n(\nu)} \nu \operatorname{Re} G(\nu), \tag{1}$$

Here c_0 is the light velocity in vacuo, $n(\nu)$ is the refraction coefficient of the pure crystal, and $G(\nu)$ is the spectral representation of the admittance $G(t)$ of a localized electron. $G(t)$ is determined through the average electron displacement $\langle x(t) \rangle$ in an external spatially uniform electric field by means of the relation^[10]

$$\langle x(t) \rangle = -ie \int_{-\infty}^{\infty} G(t-s) E(s) ds. \tag{2}$$

On the other hand

$$\begin{aligned} \langle x(t) \rangle &= \operatorname{Sp} \{ x(t) \rho(t) \} \\ &= \int x_i \delta(\mathbf{r}_i - \mathbf{r}_i') \rho(\mathbf{r}_i, \mathbf{r}_i') d\mathbf{r}_i d\mathbf{r}_i', \end{aligned} \tag{3}$$

where ρ is the density matrix.

We choose the Lagrangian of the impurity-phonon system in the form

$$\begin{aligned} L(t) &= L_e(\dot{\mathbf{r}}, \mathbf{r}, t) \\ &+ \sum_k \left[\frac{1}{2} (\dot{q}_k^2 - \omega_k^2 q_k^2) + \gamma_k(t) q_k \right], \end{aligned} \tag{4}$$

Here the first term corresponds to the motion of the electron in the field of the lattice defect, q_k are the real normal coordinates of the phonon subsystem, and $\gamma_k(t) \equiv \gamma_k(\mathbf{r}_t)$ is the force exerted by the localized electron on the k -th normal oscillator.

We assume that at the initial time $t' \rightarrow -\infty$ only the phonon subsystem is in thermal equilibrium. Following Feynman and Vernon^[9] we obtain then for the density matrix of the electron the expression

$$\rho(\mathbf{r}_{t''}, \mathbf{r}_{t'}) = \int \exp \left\{ \frac{i}{\hbar} [S_e(\mathbf{r}) - S_e(\mathbf{r}') + \Phi(\mathbf{r}, \mathbf{r}')] \right\} \times D\mathbf{r}(t) D\mathbf{r}'(t) d\mathbf{r}_t d\mathbf{r}_{t'}, \quad (5)$$

where $D\mathbf{r}(t)$ symbolizes the integration over all classic trajectories between the points \mathbf{r}_t and $\mathbf{r}_{t''}$. To each of these trajectories we juxtapose an action

$$S_e(\mathbf{r}) = \int_{t'}^{t''} [L_e(\mathbf{r}_s, \mathbf{r}_s, s) + ex_s E(s)] ds, \quad (6)$$

which includes the external electric field E .

The information on the phonon subsystem is included in the influence phase $\Phi(\mathbf{r}, \mathbf{r}')$, which is also a trajectory functional. For a set of independent harmonic oscillators we have^[8,9]

$$\begin{aligned} \Phi(\mathbf{r}, \mathbf{r}') &= \sum_h \Phi_h(\mathbf{r}, \mathbf{r}'), \\ \exp \left[\frac{i}{\hbar} \Phi_h(\mathbf{r}, \mathbf{r}') \right] &= \text{Sp} \rho_h(t'') = \int \delta(q_{ht''} - q'_{ht''}) dq_{ht''} dq'_{ht''} \\ &\times dq_{ht'} dq'_{ht'} \int \exp \left\{ \frac{i}{\hbar} \int_{t'}^{t''} [L_h(\dot{q}_{ht}, q_{ht}, \mathbf{r}_t) \right. \\ &\left. - L_h(\dot{q}'_{ht}, q'_{ht}, \mathbf{r}'_t)] dt \right\} \rho_T(q_{ht'}, q'_{ht'}) Dq_h(t) Dq'_h(t) \\ &= \exp \left(\frac{i}{2\hbar} \int_{t'}^{t''} \int dt ds [\gamma_h(t) - \gamma'_h(t)] \{ [\gamma_h(s) + \gamma'_h(s)] \right. \\ &\left. \times Y(\omega_h, t-s) + i[\gamma_h(s) - \gamma'_h(s)] A(\omega_h, t-s) \right\}. \quad (7) \end{aligned}$$

Here L_k is the Lagrangian of the harmonic oscillator perturbed by the external force $\gamma_k(t)$ [the expression in the square brackets of Eq. (4)], ρ_T is the equilibrium density matrix of the harmonic oscillator*

$$Y(\omega, t) = \begin{cases} \omega^{-1} \sin \omega t & t > 0 \\ 0 & t < 0 \end{cases}, \\ A(\omega, t) = \frac{1}{\omega} \left[\bar{n}(\omega) + \frac{1}{2} \right] \cos \omega t = \frac{1}{2\omega} \text{cth} \frac{\beta}{2} \cos \omega t,$$

and $\beta = \hbar\omega/kT$. Equation (7) is fundamental in the Lagrangian formalism of quantum statistics and will be repeatedly used in the subsequent computations. Following^[8], we introduce

$$\begin{aligned} g(t'' - t') &= \text{Sp} \rho(t'') \\ &= \int \delta(\mathbf{r}_{t''} - \mathbf{r}'_{t''}) \rho(\mathbf{r}_{t''}, \mathbf{r}'_{t''}) d\mathbf{r}_{t''} d\mathbf{r}'_{t''} \quad (8) \end{aligned}$$

with a special choice of field coefficients

$$\begin{aligned} E(s) &= \varepsilon \delta(s - t') + \eta \delta(s - t''), \\ E'(s) &= \varepsilon \delta(s - t') - \eta \delta(s - t''). \quad (9) \end{aligned}$$

The value of $\langle x(t) \rangle$ from (3) corresponding to this choice is

$$\langle x(t) \rangle = -\frac{i\hbar}{2e} \frac{\partial g(t)}{\partial \eta}.$$

Using this and substituting the first expression of (9) into (2) we obtain

$$G(t'' - t') = \frac{\hbar}{2e^2} \frac{\partial^2}{\partial \varepsilon \partial \eta} g(t'' - t') \Big|_{\varepsilon=\eta=0}. \quad (10)$$

The problem is therefore reduced to the calculation of

$$\begin{aligned} g(t'' - t') &= \int \delta(\mathbf{r}_{t''} - \mathbf{r}'_{t''}) d\mathbf{r}_{t''} d\mathbf{r}'_{t''} d\mathbf{r}_t d\mathbf{r}_{t'} \\ &\times \int \exp \left[\frac{i}{\hbar} F(\mathbf{r}, \mathbf{r}') \right] D\mathbf{r}(t) D\mathbf{r}'(t), \quad (11) \end{aligned}$$

where F designates the argument of the exponential in (5).

Proceeding to the Fourier representation we obtain an exact expression for the admittance $G(\nu)$. One has to bear in mind, of course, that the continual integration in (11) is feasible only when the functional in the exponent is quadratic in the velocities and coordinates^[11]. Thus, the method described is of practical value only when the approximation of the system by a functional of the denoted kind is good.

2. THE APPROXIMATION METHOD, ZEROth APPROXIMATION

Consider an ionic crystal with a local hydrogen-like center. Assuming the radius of the electron state large enough, we can regard the crystal as an isotropic dielectric continuum, and take into account only the interaction of the electron with the longitudinal optical phonons, disregarding their frequency dispersion. For electron states with large radii the effective charge of the Coulomb center is e/ϵ_0 , ϵ_0 being the static dielectric constant. In this case (see, e.g.,^[7]) the summation of the influence phases (7) is exact, and we obtain

$$\begin{aligned} F(\mathbf{r}, \mathbf{r}') &= \frac{\mu}{2} \int_{-\infty}^{\infty} (\mathbf{r}_t^2 - \mathbf{r}'_t{}^2) dt + \frac{e^2}{\epsilon_0} \int_{-\infty}^{\infty} \left(\frac{1}{|\mathbf{r}_t|} - \frac{1}{|\mathbf{r}'_t|} \right) dt \\ &+ e \int_{-\infty}^{\infty} [E(t)x_t - E'(t)x'_t] dt \\ &+ \alpha \hbar \omega^2 \left(\frac{\hbar \omega}{2\mu} \right)^{1/2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dt ds \left[f(\omega, t-s) \right. \\ &\times \left(\frac{1}{|\mathbf{r}_t - \mathbf{r}_s|} - \frac{1}{|\mathbf{r}'_t - \mathbf{r}_s|} \right) \\ &\left. + f^*(\omega, t-s) \left(\frac{1}{|\mathbf{r}_t - \mathbf{r}'_s|} - \frac{1}{|\mathbf{r}'_t - \mathbf{r}'_s|} \right) \right]. \quad (12) \end{aligned}$$

* $\text{cth} \equiv \text{coth}$.

Here

$$f(\omega, t) = Y(\omega, t) + iA(\omega, t)$$

α is the electron-phonon coupling constant,

$$\alpha = \left(\frac{\mu e^4}{2\hbar^3 \omega} \right)^{1/2} \left(\frac{1}{n^2} - \frac{1}{\epsilon_0} \right) \quad (13)$$

μ is the effective mass of the band electron, and ω is the limiting frequency of the longitudinal optical phonons.

It was shown previously^[6,7] that in the calculations of the ground state energy and of the thermodynamic functions of an ionic crystal with a hydrogen-like local center, a good approximation is achieved with the trial Lagrangian

$$L_0(t) = 1/2\mu\dot{\mathbf{r}}^2 - 1/2\mu u^2 \mathbf{r}^2 + 1/2M\dot{\mathbf{R}}^2 - 1/2Mw^2(\mathbf{R} - \mathbf{r})^2, \quad (14)$$

in which the Coulomb field of the defect is imitated by a three-dimensional parabolic potential, and the polaron effect—by introducing a fictitious particle of mass M , which is elastically bound to the electron. In Eq. (14), M , u , and w are parameters determined from the variational principle for the partition function^[7]. Neglecting their dependence on the weak external electric field one may hope that the transition from the Lagrangian (4) to the trial Lagrangian (14) will be a good approximation also for the calculation of the non-equilibrium density matrix. Accordingly, in the zeroth approximation we replace g by

$$g_0(t'' - t') = \int \delta(\mathbf{r}_{t''} - \mathbf{r}'_{t'}) d\mathbf{r}_{t''} d\mathbf{r}'_{t'} d\mathbf{r}_t d\mathbf{r}'_t \\ \times \int \exp \left[\frac{i}{\hbar} F_0(\mathbf{r}, \mathbf{r}') \right] D\mathbf{r}(t) D\mathbf{r}'(t), \quad (15)$$

where F_0 includes the influence phase of the \mathbf{R} -particle calculated from Eq. (7). Omitting the details of calculation, we present the final formula:

$$F_0(\mathbf{r}, \mathbf{r}') = \frac{\mu}{2} \int_{-\infty}^{\infty} (\dot{\mathbf{r}}_t^2 - \dot{\mathbf{r}}_t'^2) dt \\ - \frac{1}{2}(\mu u^2 + Mw^2) \int_{-\infty}^{\infty} (\mathbf{r}_t^2 - \mathbf{r}_t'^2) dt \\ + e \int_{-\infty}^{\infty} [E(t)x_t - E'(t)x_t'] dt + \frac{Mw^4}{2} \int_{-\infty}^{\infty} dt ds \\ \times [f(w, t-s)(\mathbf{r}_t - \mathbf{r}_t', \mathbf{r}_s) + f^*(w, t-s)(\mathbf{r}_t - \mathbf{r}_t', \mathbf{r}_s')]. \quad (16)$$

The double continual integral in (15) can be evaluated exactly. This is easiest to do by introducing the normal coordinates ρ_1 and ρ_2 of the trial system by means of the transformation

$$\mathbf{r} = (a_1/\mu)^{1/2}\rho_1 - (a_2/\mu)^{1/2}\rho_2, \\ \mathbf{R} = \frac{w^2}{w^2 - v_1^2} \left(\frac{a_1}{\mu} \right)^{1/2} \rho_1 + \frac{w^2}{v_2^2 - w^2} \left(\frac{a_2}{\mu} \right)^{1/2} \rho_2; \quad (17)$$

$$a_1 = (w^2 - v_1^2) / (v_2^2 - v_1^2),$$

$$a_2 = (v_2^2 - w^2) / (v_2^2 - v_1^2), \quad (18)$$

where v_1^2 and v_2^2 are the roots of equation

$$v^4 - v^2(\lambda^2 w^2 + u^2) + u^2 w^2 = 0, \quad \lambda^2 = 1 + M/\mu. \quad (19)$$

The double continual integral (15) transforms then into a product of two standard continual integrals (7) for oscillators under the action of two external forces $e\mathbf{E}(a_1/\mu)^{1/2}$ and $-e\mathbf{E}(a_2/\mu)^{1/2}$, respectively. After the evaluation of these integrals we transform to the spectral representation to obtain

$$g_0 = \exp \left(\frac{ie^2}{4\pi\hbar} \int_{-\infty}^{\infty} [\mathbf{E}(-\nu) - \mathbf{E}'(-\nu)] \{ [\mathbf{E}(\nu) + \mathbf{E}'(\nu)] Y_0(\nu) \right. \\ \left. + i[\mathbf{E}(\nu) - \mathbf{E}'(\nu)] A_0(\nu) \} d\nu \right), \quad (20)$$

$$\mathbf{E}(\nu) = \int_{-\infty}^{\infty} \mathbf{E}(t) e^{-i\nu t} dt, \quad (21)$$

$$Y_0(\nu) = (w^2 - \nu^2) / \mu [v_1^2 - (\nu - i0)^2] [v_2^2 - (\nu - i0)^2], \quad (22)$$

$$A_0(\nu) = \left(\frac{\pi}{2\mu} \right) \sum_{i=1,2} \frac{a_i}{v_i} \text{cth} \frac{\beta_i}{2} [\delta(\nu - v_i) + \delta(\nu + v_i)], \quad (23)$$

$$\beta_i = \hbar v_i / kT.$$

Substituting (9) into (20) and (21) and calculating G_0 from (10) we get

$$G_0(t'' - t') = \frac{i}{2\pi} \int_{-\infty}^{\infty} e^{i\nu(t'' - t')} Y_0(\nu) d\nu, \quad (24)$$

from which immediately follows

$$G_0(\nu) = iY_0(\nu). \quad (25)$$

Substituting (25) and (22) in (1) we obtain the expression for the impurity light absorption coefficient in the zeroth approximation

$$\kappa_0(\nu) = \frac{\pi^2 N}{n(\nu)} \frac{e^2}{\mu c_0} [a_1 \delta(\nu - v_1) + a_2 \delta(\nu - v_2)]. \quad (26)$$

Thus, in the zeroth approximation the absorbed frequencies are equal to the normal modes v_1 and v_2 of the trial system.

3. FIRST ORDER CORRECTION, ONE-PHONON LINES

Let us write (11) in the form

$$g = \int \delta(\mathbf{r}_{t''} - \mathbf{r}'_{t'}) d\mathbf{r}_{t''} d\mathbf{r}'_{t'} d\mathbf{r}_t d\mathbf{r}'_t \int e^{iF_0/\hbar} e^{i(F-F_0)/\hbar} D\mathbf{r} D\mathbf{r}' \\ = g_0 \left\{ 1 + \frac{i}{\hbar} \langle F - F_0 \rangle_0 \right. \\ \left. + \frac{1}{2!} \left(\frac{i}{\hbar} \right)^2 \langle (F - F_0)^2 \rangle_0 + \dots \right\}, \quad (27)$$

where the continual average of the trajectory functional is defined by the expression

$$\langle A \rangle_0 = g_0^{-1} \int \delta(\mathbf{r}_{t''} - \mathbf{r}'_{t''}) d\mathbf{r}_{t''} d\mathbf{r}'_{t''} d\mathbf{r}_t d\mathbf{r}'_t \times \int A(\mathbf{r}, \mathbf{r}') \exp \left\{ \frac{i}{\hbar} F_0(\mathbf{r}, \mathbf{r}') \right\} D\mathbf{r} D\mathbf{r}' \quad (28)$$

In (27) we restrict ourselves to the first order correction and introduce four generating functions of the type

$$\Psi_{\mathbf{K}}^{(1)}(x, y) = \langle \exp(i\mathbf{K}, x\mathbf{r}_t - y\mathbf{r}_s) \rangle_0 \quad (29)$$

The other three functions are obtained from (29) by replacing $\mathbf{r}_t, \mathbf{r}_s$, or both by \mathbf{r}'_t and \mathbf{r}'_s , respectively. The generating functions (29) are calculated in the same way as g_0 : after the transformation (17) to normal coordinates, (29) turns into a product of standard traces of the type (7). Several such transformations yield

$$\begin{aligned} \ln \Psi_{\mathbf{K}}^{(1)}(x, y) &= \frac{ieK_1}{2\pi} \varepsilon \int_{-\infty}^{\infty} dv [xe^{iv(t-t')} - ye^{iv(s-t')}] Y_0(v) \\ &+ \frac{ieK_1}{2\pi} \eta \int_{-\infty}^{\infty} dv \{ [xe^{iv(t''-t)} - ye^{iv(t''-s)}] [Y_0(v) + iA_0(v)] \\ &+ i [xe^{iv(t-t'')} - ye^{iv(s-t'')}] A_0(v) \} \\ &+ \frac{i\hbar K^2}{4\pi} \int_{-\infty}^{\infty} dv [x^2 + y^2 - 2xy \cos v(t-s)] [Y_0(v) + iA_0(v)]. \end{aligned} \quad (30)$$

Similar expressions are obtained for the remaining generating functions.

The mean values (in the sense of Eq. (28)) of all the quantities contained in $\langle F - F_0 \rangle_0$ are obtained from the generating functions by simple operations. For example

$$\langle |\mathbf{r}_t - \mathbf{r}_s|^{-1} \rangle_0 = \frac{1}{2\pi^2} \int \Psi_{\mathbf{K}}^{(1)}(x, y) \frac{d\mathbf{K}}{K^2} \Big|_{x=y=1}, \quad (31a)$$

$$\langle |\mathbf{r}_t|^{-1} \rangle_0 = \frac{1}{2\pi^2} \int \Psi_{\mathbf{K}}^{(1)}(x, y) \frac{d\mathbf{K}}{K^2} \Big|_{\substack{x=1 \\ y=0}}, \quad (31b)$$

$$\langle (\mathbf{r}_t, \mathbf{r}_s) \rangle_0 = \frac{\partial^2}{\partial x \partial y} \sum_{i=1}^3 \frac{1}{K_i^2} \Psi_{\mathbf{K}_i}^{(1)}(x, y) \Big|_{x=y=0}. \quad (31c)$$

In (30) and (31c), K_1, K_2, K_3 are the projections of \mathbf{K} on the Cartesian coordinate axes, one of which (K_1) is in the external field direction. $\Psi_{\mathbf{K}_i}$ are the responding factors in the generating function (30).

The operations (31), the differentiation with respect to ϵ and η in (10), as well as the transition to the spectral representation can be performed in any sequence; this simplifies the subsequent calculations. Let us take, for example,

$$\begin{aligned} G_1^{(1)}(t'' - t') &= \frac{i}{2c^2} \frac{\partial^2}{\partial \epsilon \partial \eta} \left\{ g_0 a \hbar \omega^2 \left(\frac{\hbar \omega}{2\mu} \right)^{1/2} \right. \\ &\times \left. \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dt ds f(\omega, t-s) \langle |\mathbf{r}_t - \mathbf{r}_s|^{-1} \rangle_0 \right\} \Big|_{\epsilon=\eta=0}. \end{aligned} \quad (32)$$

It follows from (19) that for $\epsilon = \eta = 0, g_0 = 1, \partial g_0 / \partial \epsilon = \partial g_0 / \partial \eta = 0$. It can be shown that $g_1 \equiv (i/\hbar) g_0 \langle F - F_0 \rangle_0 = 0$ for $\epsilon = \eta = 0$; therefore in $G_1(\nu)$ the contribution of terms containing $\partial^2 g_0 / \partial \epsilon \partial \eta$ equals zero. Thus, (32) can be rewritten in the form

$$\begin{aligned} G_1^{(1)}(t'' - t') &= \frac{i\alpha \hbar \omega^2}{2e^2} \left(\frac{\hbar \omega}{2\mu} \right)^{1/2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dt ds f(\omega, t-s) \\ &\times \frac{1}{2\pi^2} \int \frac{d\mathbf{K}}{K^2} \frac{\partial^2 \Psi_{\mathbf{K}}^{(1)}(1, 1)}{\partial \epsilon \partial \eta} \Big|_{\epsilon=\eta=0}. \end{aligned}$$

After the substitution of (30) and simple transformations, we obtain

$$\begin{aligned} G_1^{(1)}(t'' - t') &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dv e^{iv(t''-t')} \left\{ -\frac{ia\hbar\omega^2}{2\pi^2} \left(\frac{\hbar\omega}{2\mu} \right)^{1/2} Y_0(v) \right. \\ &\times [Y_0(v) + 2iA_0(v)] \int_{-\infty}^{\infty} d\vartheta (1 - \cos v\vartheta) f(\omega, \vartheta) \int \frac{K_1^2}{K^2} d\mathbf{K} \\ &\times \left. \exp \left[\frac{i\hbar K^2}{2\pi} \int_{-\infty}^{\infty} (1 - \cos \mu\vartheta) (Y_0(\mu) + iA_0(\mu)) d\mu \right] \right\}. \end{aligned}$$

Using the features of the functions $Y_0(\nu)$ and $A_0(\nu)$, (Eqs. (22, 23)) and proceeding to the spectral representation, we obtain

$$\begin{aligned} G_1^{(1)}(v) &= \frac{\alpha}{3\sqrt{\pi}} \left(\frac{\omega}{\hbar} \right)^{3/2} \frac{1}{\mu \operatorname{sh}(\beta/2)} Y_0(v) [Y_0(v) + 2iA_0(v)] \\ &\times \int_0^{\infty} d\vartheta (1 - \cos v\vartheta) \cos \left(\omega\vartheta + \frac{i\beta}{2} \right) [D_0^*(\vartheta)]^{-3/2}, \end{aligned} \quad (33)^*$$

$$D_0(\vartheta) = \frac{1}{\mu \hbar} \sum_{j=1,2} \frac{a_j}{v_j} \left[\operatorname{cth} \frac{\beta_j}{2} - \frac{\cos(v_j\vartheta + i\beta_j/2)}{\operatorname{sh}(\beta_j/2)} \right]. \quad (34)$$

The other quantities in g_1 are calculated similarly. The final expression for the first-order term in the expansion of $G(\nu)$ is

$$G_1(v) = -iY_0^2(v) \left\{ \chi_0(v) + \frac{4}{3\sqrt{\pi}} \frac{e^2}{\varepsilon_0} \left(\frac{\mu}{\hbar} \right)^{3/2} \zeta^{-3/2} + B(v) \right\}, \quad (35)$$

$$\begin{aligned} \chi_0(v) &= \frac{2\alpha}{3\sqrt{\pi}} \left(\frac{\omega}{\hbar} \right)^{3/2} \frac{1}{\mu \operatorname{sh}(\beta/2)} \int_0^{\infty} (1 - e^{-iv\vartheta}) \\ &\times \operatorname{Im} \left\{ \cos \left(\omega\vartheta - \frac{i\beta}{2} \right) [D_0(\vartheta)]^{-3/2} \right\} d\vartheta, \end{aligned} \quad (36)$$

$$\zeta = \sum_{i=1,2} \frac{a_i}{v_i} \operatorname{cth} \frac{\beta_i}{2}, \quad (37)$$

$$B(v) = \frac{\mu}{[w^2 - (v - i0)^2]} [v^2(v_1^2 - w^2) - v_2^2(v_1^2 - v^2)]. \quad (38)$$

In the general case $\chi_0(\nu)$ can be computed only numerically. However, confining ourselves to the low-temperature case ($\beta > 1$) and to large v_1 and v_2 (in comparison with ω), we can expand the inte-

*sh \equiv sinh.

grand (36) in a series. In the first approximation we obtain

$$\begin{aligned} \chi_0'(v) \equiv \text{Re } \chi_0(v) &= \frac{\alpha\mu}{3\sqrt{\pi}} \left(\frac{\omega}{\zeta}\right)^{3/2} \\ &\times \left\{ \frac{2}{\omega} + \frac{1}{v-\omega} - \frac{1}{v+\omega} + \frac{3}{4\zeta \text{sh}(\beta/2)} \right. \\ &\times \sum_{i=1,2} \frac{a_i}{v_i \text{sh}(\beta_i/2)} \left[\text{sh} \frac{\beta_i + \beta}{2} \left(\frac{2}{v_i + \omega} + \frac{1}{v - v_i - \omega} \right. \right. \\ &\left. \left. - \frac{1}{v + v_i + \omega} \right) + \text{sh} \frac{\beta_i - \beta}{2} \left(\frac{2}{v_i - \omega} \right. \right. \\ &\left. \left. + \frac{1}{v - v_i + \omega} - \frac{1}{v + v_i - \omega} \right) \right] \right\}, \quad (39) \end{aligned}$$

where all fractions should be understood in the sense of the principal value

$$\begin{aligned} \chi_0''(v) \equiv \text{Im } \chi_0(v) &= \frac{\alpha\mu\sqrt{\pi}}{3} \left(\frac{\omega}{\zeta}\right)^{3/2} \left\{ \delta(v-\omega) - \delta(v+\omega) \right. \\ &+ \frac{3}{4\zeta \text{sh}(\beta/2)} \sum_{i=1,2} \frac{a_i}{v_i \text{sh}(\beta_i/2)} \left[\text{sh} \frac{\beta_i + \beta}{2} (\delta(v - v_i - \omega) \right. \\ &\left. - \delta(v + v_i + \omega)) + \text{sh} \frac{\beta_i - \beta}{2} (\delta(v - v_i + \omega) \right. \\ &\left. - \delta(v + v_i - \omega)) \right] \left. \right\}. \quad (40) \end{aligned}$$

Now, taking into account the properties of the singular functions $Y_0(\nu)$, $\chi_0(\nu)$, and $B(\nu)$, we find

$$\begin{aligned} \text{Re } G_1(v) &= Y_0''(v) \chi_0''(v) + 2Y_0'(v) Y_0''(v) \\ &\times \left[\chi_0'(v) + \frac{4}{3\sqrt{\pi}} \frac{e^2}{\epsilon_0} \left(\frac{\mu}{\hbar}\right)^{3/2} \zeta^{-3/2} + B'(v) \right]. \quad (41) \end{aligned}$$

Upon substitution in (1), the quantity (41) contributes to the impurity absorption coefficient

$$\begin{aligned} \kappa_1(v) &= \frac{2\pi N e^2}{c_0 n(v)} \sum_{i=1,2} b_i v_i \left\{ \frac{\pi}{\mu} v_i^2 - \frac{4\sqrt{2\pi}}{3\mu} \frac{\alpha}{\epsilon_0 c} \omega^{1/2} \zeta^{-3/2} \right. \\ &- \frac{2\sqrt{\pi}\alpha}{3\mu} \left(\frac{\omega}{\zeta}\right)^{3/2} v_i^2 \left[\frac{1}{\omega(v_i^2 - \omega^2)} \right. \\ &+ \frac{3}{4\zeta \text{sh}(\beta/2)} \sum_{j=1,2} \frac{a_j}{v_j \text{sh}(\beta_j/2)} \\ &\times \left(\frac{\text{sh}[(\beta_j + \beta)/2]}{(v_j + \omega)[v_i^2 - (v_j + \omega)^2]} \right. \\ &\left. \left. + \frac{\text{sh}[(\beta_j - \beta)/2]}{(v_j - \omega)[v_i^2 - (v_j - \omega)^2]} \right) \right] \left. \right\} \delta(v - v_i) \\ &+ \frac{2\pi^{3/2} N e^2 \alpha}{3c_0 n(v) \mu} \left(\frac{\omega}{\zeta}\right)^{3/2} \left\{ \frac{3}{4\zeta \text{sh}(\beta/2)} \sum_{i=1,2} \frac{a_i}{v_i \text{sh}(\beta_i/2)} \right. \\ &\times \left[\frac{(v_i + \omega)[\omega^2 - (v_i + \omega)^2]^2}{[v_1^2 - (v_i - \omega)^2]^2 [v_2^2 - (v_i - \omega)^2]^2} \right. \\ &\left. \times \text{sh}[(\beta_i + \beta)/2] \delta(v - v_i - \omega) \right. \end{aligned}$$

$$\begin{aligned} &+ \frac{|v_i - \omega|[\omega^2 - (v_i - \omega)^2]^2}{[v_1^2 - (v_i - \omega)^2]^2 [v_2^2 - (v_i - \omega)^2]^2} \\ &\times \text{sh} [|\beta_i - \beta|/2] \delta(v - |v_i - \omega|) \left. \right] \\ &+ \frac{\omega(\omega^2 - \omega^2)^2}{(v_1^2 - \omega^2)^2 (v_2^2 - \omega^2)^2} \delta(v - \omega) \left. \right\}; \quad (42) \end{aligned}$$

$$\begin{aligned} c &= \frac{1}{n^2} - \frac{1}{\epsilon_0}, \quad b_1 = \frac{a_1}{v_1} \left(\frac{a_1}{4v_1^2} + \frac{a_2}{v_2^2 - v_1^2} \right), \\ b_2 &= \frac{a_2}{v_2} \left(\frac{a_2}{4v_2^2} + \frac{a_1}{v_1^2 - v_2^2} \right). \end{aligned}$$

The first two terms of this expression represent the first-order corrections to the intensities of the no-phonon lines (26). The subsequent terms describe the one-phonon lines corresponding to transitions in which the excitation of the normal mode $v_{1(2)}$ of the trial system is accompanied by the generation or absorption of a phonon. Finally, the last term in (42) characterizes the additional lattice absorption stimulated by the impurity-phonon interaction.

Returning to (39) and (40), we note that allowance for higher order terms in the expansion of the integrand (36) leads to the appearance of additional absorption lines at the frequencies $2v_1 \pm \omega$, $2v_2 \pm \omega$, and $|v_1 \pm v_2| \pm \omega$, and also to the appearance of additional small corrections to the intensities of the no-phonon lines. The two-phonon and higher phonon-number transitions can be obtained by taking into account the subsequent terms in the expansion of (27). The calculation of the multi-phonon line intensities in the outlined way does not offer basic difficulties but calls for tremendously cumbersome transformations. Such calculations are hardly justified: when the terms of the series (27) rise to a certain $n > 1$ we obtain the case of large heat release^[3], for which the criteria of the adiabatic approximation are fulfilled. Conversely, if the series (27) converges beginning from the first term (the case of small heat release), then the foregoing no-phonon and one-phonon lines play the main role in the impurity absorption spectrum. We emphasize that small heat release can be realized also in the case of intermediate (and not only weak) polaron binding.

4. THE CASE OF STRONG LOCAL BINDING. DISCUSSION OF RESULTS

It was shown earlier^[7] that in a broad range of the coupling constant α the parameters of the trial Lagrangian (14) satisfy the inequality

$$u^2 \gg \lambda^2 \omega^2, \quad (43)$$

which corresponds to the case of strong binding of the electron with the lattice defect. In this case one obtains from (19) $v_1^2 \cong w^2$, and it is easily seen that the parameters v_1 and w drop out from the formulae of the theory. The remaining parameter v_2 is determined from the equation

$$\frac{3}{2} \left(\frac{v_2}{\omega} \right)^{3/2} - \frac{\alpha}{\sqrt{\pi}} \left(1 + \frac{2\sqrt{2}}{\epsilon_0 c} \right) \frac{v_2}{\omega} + \frac{2\alpha \ln 2}{\sqrt{\pi}} \operatorname{cth} \frac{\beta}{2} = 0, \quad (44)$$

which is derived from the variational principle of the partition function. Equation (44) is valid at low temperatures when $\beta_2 \gg 1$. The integral intensities of the no-phonon line and of the one-phonon peaks are expressed in terms of v_2 by the equations

$$J_0 = \frac{\pi^2 N}{n(\nu)} \frac{e^2}{\mu c_0} (1 + \gamma), \quad (45)$$

$$J_{1^{(+)}} = \frac{\pi^{3/2} N}{n(\nu)} \frac{e^2}{\mu c_0} \alpha \frac{v_2^{3/2} (v_2 + \omega)}{\omega^{1/2} (2v_2 + \omega)^2} [\bar{n}(\omega) + 1] \quad (46)$$

$$J_{1^{(-)}} = \frac{\pi^{3/2} N}{n(\nu)} \frac{e^2}{\mu c_0} \alpha \frac{v_2^{3/2} (v_2 - \omega)}{\omega^{1/2} (2v_2 - \omega)^2} \bar{n}(\omega), \quad (47)$$

where γ allows for the contribution of expression (42) in the no-phonon line.

Since the absolute values of the intensities depend on the concentration of the impurity centers, which is not always amenable to accurate experimental determination, the relative intensity S of the one-phonon peak

$$S = J_{1^{(+)}} / J_0 \quad (48)$$

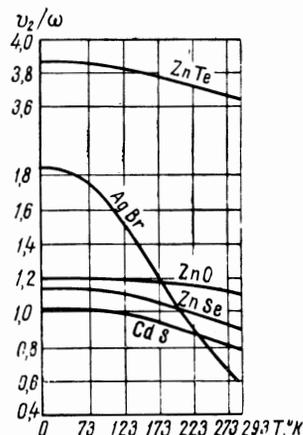
is of interest. For $T = 0$ and $v_2 \gg \omega$ Eq. (48) becomes

$$S = \frac{\alpha^2}{6\pi(1+\gamma)} \left(1 + \frac{2\sqrt{2}}{\epsilon_0 c} \right), \quad (49)$$

$$\gamma = \frac{3}{8(1 + 2\sqrt{2}/\epsilon_0 c)}. \quad (50)$$

The values of S calculated from Eq. (49) for some ionic crystals are listed in the table. Next to the chemical formulae of each crystal we indicate the reference from which the values of ω , ϵ_0 , n^2 , and μ have been taken. For crystals with $\alpha \lesssim 1$ we get correspondingly $S < 1$ and the case of small heat release is realized. For $\alpha \gg 1$ (alkali-halide crystals) we have $S \gg 1$ (large heat release). In this case, as already pointed out, one has to use the adiabatic theory of the impurity absorption.

	$\hbar\omega \cdot 10^3$, eV	$\epsilon_0 c$	α	S
NaCl [12]	3.22	1.49	8.80	10.54
KCl [12]	2.62	1.20	7.77	9.677
AgBr [5]	1.80	1.70	1.67	0.346
ZnO [13,14,15]	7.3	1.28	1.16	0.205
CdS [6]	3.8	0.704	0.65	0.106
ZnSe [16]	3.14	0.409	0.41	0.0664
ZnTe [16]	2.59	0.223	0.39	0.108



The temperature dependence of the location of the no-phonon and one-phonon peaks is given by Eq. (44). Solving this equation by successive approximations we obtain

$$\sqrt{v_2} = \frac{2\alpha\sqrt{\omega}}{3\sqrt{\pi}} \left(1 + \frac{2\sqrt{2}}{\epsilon_0 c} \right) \left[1 - \frac{9\pi \ln 2 \operatorname{cth}(\beta/2)}{2\alpha^2(1 + 2\sqrt{2}/\epsilon_0 c)^3} \right]. \quad (51)$$

The figure shows the temperature dependence of v_2 calculated from (51) for a number of ionic crystals. The curves show that for $\alpha \lesssim 1$ the criterion for the applicability of Eqs. (49)–(51) is fulfilled only for ZnTe. In the other crystals considered $v_2 \approx \omega$ at low temperatures. We notice, however, that a calculation of the ground state energy [7] demonstrates the low sensitivity of the theory to the violation of the aforementioned criterion.

For the intensity of the excess absorption (above the intrinsic infrared lattice absorption) we get at $\nu = \omega$

$$J_\omega = \frac{2\pi^{3/2} N}{3n(\nu)} \frac{e^2}{\mu c_0} \alpha \frac{\omega^{5/2} v_2^{3/2}}{(v_2^2 - \omega^2)^2} \left(\operatorname{cth} \frac{\beta_2}{2} \right)^{-3/2}. \quad (52)$$

This equation may possibly be used to determine the concentration of the impurity centers by comparing the lattice absorption intensities of the pure and impure crystals.

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