SOVIET PHYSICS JETP VOLUME 14, NUMBER 6 JUNE, 1962

SLOW ELECTRONS IN POLAR CRYSTALS

A. V. TULUB

Leningrad State University

Submitted to JETP editor March 23, 1961

J. Exptl. Theoret. Phys. (U.S.S.R.) **41**, 1828-1838 (December, 1961)

We have considered the interaction between a non-relativistic particle and a scalar field and have applied the theory to the polaron problem. We use a Lee, Low, and Pines canonical transformation to obtain from the Hamiltonian of the system an effective Hamiltonian; we solve the corresponding Heisenberg equations of motion. The energy is obtained from a variational principle for arbitrary values of the coupling constant. We consider, moreover, the scattering of polarons by phonons as a resonance scattering process; we evaluate the value of the resonance momentum in the strong coupling region. The strong dependence on the coupling constant g which is characteristic for the resonance momentum leads to an upper limit of g^2 of about 8 or 9.

THE electrons in polar crystals create around themselves a localized polarization of the ionic lattice, which accompanies the electrons when they are transferred to the conduction band. If the dimensions of this polarization are sufficiently large, one can, according to Pekar,[1] consider the crystal in the continuous-medium approximation, taking the periodic field of the lattice into account by introducing an effective electron mass m. The latter appears as a basic, unknown parameter in the whole theory, and ultimately determines the magnitude of the coupling constant g for the electron-phonon interaction. This constant is, as a rule, insufficiently small to justify the usual perturbation theory, at least of the first perturbation-theory approximation.

The simplest and most reliable method for determining the effective mass consists in studying the mobilities of the current carriers, which at the present time are already known experimentally for a number of polar crystals. To solve this problem we need know the mobility as a function of the coupling constant for a wide range of coupling constants. For most polar crystals the intermediate coupling range is apparently of most interest; this range is at the same time the most complicated one from a theoretical point of view and the one for which there are in the literature greatly contradictory calculations.[2,3] When solving the problem of the mobility it is natural to start from two extreme approximations in the polaron theory, the weak and strong coupling approximations, with the aim of a subsequent extrapolation of the mobility values found in these regions to the intermediate coupling region.

The scattering of optical phonons by a polaron is a typical problem in resonance scattering;[2,3] when evaluating the scattering amplitude it is convenient to start from Low's well-known method;[4] to apply this method we need know the explicit form of the eigenfunctionals of the polaron in the initial and final states in a form sufficiently convenient for the calculation. In this connection, we develop in the first part of this paper a new method for solving the polaron problem.

A study of the mobility is also of interest because it provides an opportunity to establish the limits of applicability of the whole polaron theory as a physical problem, since the condition for the existence of scattering of polarons by optical phonons is at the same time also the condition that limits the maximum possible coupling-constant values permitted in the theory. Indeed, when the coupling constant increases, the effective dimensions of the polaron decrease, and at the same time the wavelength of the vibrations of the crystalline lattice, which are responsible for the scattering, also decreases. The latter, moreover, cannot be less than a quantity of the order of the dimensions of the elementary cell, so that not all a priori chosen coupling constants are permissible in a real physical problem. Even if we make the most extreme assumption that the whole of the polaron mobility is connected with the scattering by the shortest waves existing in the crystal, it turns out that the maximum coupling constant corresponding to this scattering is approximately equal to $g_{\max}^2 \approx 8$ to 9.

These values lie at the border of applicability of the strong-coupling formulae; the situation is thus just the opposite of the one assumed to occur in the first papers on polaron theory: it seems unlikely that there are polar crystals with strong coupling and at the same time with anomalously large effective polaron mass characteristic of strong coupling. A proof of this statement will be given in the second part of this paper, in which we consider the scattering theory in the strong-coupling region.

1. STATEMENT OF THE PROBLEM AND BASIC EQUATIONS

The polaron energy operator can be written in the second-quantization representation in the form

$$H = -\frac{\hbar^2\nabla^2}{2m} + \sum_k \hbar\omega_k^0 a_k^+ a_k + \sum_k V_k (a_k e^{i\mathbf{kr}} + a_k^+ e^{-i\mathbf{kr}}), \quad (1.1)$$

where a_k and a_k^+ are the phonon field operators, m the effective mass, and ω_k^0 the frequency of the longitudinal optical phonons; the function V_k is of the form

$$V_k = \frac{\hbar\omega_k^0}{k} g \left(\frac{4\pi}{uL^3}\right)^{1/2}, \quad u = \sqrt{\frac{2m\omega_k^0}{\hbar}}, \quad (1.2)$$

where g is the coupling constant,

$$g^2 = \frac{e^2}{2\hbar\omega_k^0} u \left(\frac{1}{n^2} - \frac{1}{\varepsilon}\right), \quad (1.3)$$

ϵ is the static dielectric constant, and n the refractive index for light.

For polar crystals a typical situation is one where ϵ, n, and ω_k^0 are known sufficiently accurately and the only unknown quantity is the effective mass m, which at the same time determines the value of g:

$$g^2 = g_0^2 (m/m_0)^{1/2}, \quad (1.4)$$

where g_0^2 is the value of the coupling constant for the case where the effective mass is equal to the electron mass in vacuo, m_0.

It is well known that we can eliminate the electron coordinates from (1.2) by using the canonical transformation

$$S = \exp\left\{\frac{i}{\hbar}\left(\mathbf{P} - \sum_k \hbar\mathbf{k} a_k^+ a_k\right)\mathbf{r}\right\}, \quad (1.5)$$

where **P** is the total momentum of the system.

Having transformed the energy operator using (1.5), we follow Lee, Low, and Pines[5] and subject it to one more canonical transformation:

$$U = \exp\left\{\sum_k f_k (a_k - a_k^+)\right\}, \quad (1.6)$$

where f_k is a function of k and $(\mathbf{k}\cdot\mathbf{P})$. We can write the operator obtained after the transformations (1.5) and (1.6) in the form

$$H = H_0 + H_\mathrm{I}, \quad (1.7)$$

where we take for the effective Hamiltonian H_0[6] the expression

$$H_0 = \frac{\mathbf{P}^2}{2m} + 2\sum_k V_k f_k + \sum_k \left(\hbar\omega_k^0 - \frac{\hbar\mathbf{kP}}{m}\right) f_k^2 + \frac{1}{2m}\left(\sum_k \mathbf{k} f_k^2\right)^2 + \mathcal{H}_0, \quad (1.8)$$

$$\mathcal{H}_0 = \sum_k \hbar\omega_k(\mathbf{P}) a_k^+ a_k + \frac{1}{2m}\sum_{k,k'} \mathbf{kk}' f_k f_{k'} (a_k a_{k'} + a_k^+ a_{k'}^+ + a_k^+ a_{k'} + a_{k'}^+ a_k), \quad (1.9)$$

while the operator H_1 is of the form

$$H_\mathrm{I} = \sum_k (V_k + f_k \cdot \hbar\omega_k(\mathbf{P}))(a_k + a_k^+) + \sum_{k,k'} \frac{\mathbf{kk}'}{m} f_{k'} (a_k^+ a_k a_{k'} + a_k^+ a_{k'}^+ a_k) + \frac{1}{2m}\sum_{k,k'} \mathbf{kk}' a_k^+ a_{k'}^+ a_k a_{k'}; \quad (1.10)$$

$$\hbar\omega_k(\mathbf{P}) \equiv \hbar\omega_k^0 - \frac{\hbar\mathbf{k}}{m}\mathbf{P} + \frac{\hbar^2 k^2}{2m} + \frac{\hbar\mathbf{k}}{m}\sum_{k'} \hbar\mathbf{k}' f_{k'}^2. \quad (1.11)$$

The operator $\mathcal{H}_0$ is a quadratic expression in the phonon absorption and annihilation operators and can be diagonalized in the usual way. If we denote by ν_k the frequencies of the normal vibrations we can write the required polaron self-energy ΔE in the form*

$$\Delta E = \frac{1}{2}\sum_k (\nu_k - \omega_k) = -\frac{1}{8\pi i}\int_C \frac{ds}{\sqrt{s}} \ln \Delta(s), \quad (1.12)$$

where we have denoted by $\Delta(s)$ the quantity

$$\Delta(s) = \prod_k (s - \nu_k^2) \Big/ \prod_k (s - \omega_k^2), \quad (1.13)$$

and the integration contour C is in the complex s-plane (Fig. 1). One can show that

$$\Delta(s) = \prod_{i=1}^{3} D^{(i)}(s), \quad (1.14)$$

$$D^{(i)}(s) = 1 - \frac{2}{(2\pi)^3}\int \frac{k_i^2 f_k^2 \omega_k}{s - \omega_k^2} d\mathbf{k}. \quad (1.15)$$

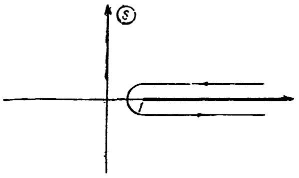

FIG. 1

---

*In the following we put $\hbar = 1$, and in Secs. 1 and 2 also $\omega_k^0 = 1$.

From (1.12) and (1.14) we get for the particular case where $\mathbf{P} = 0$, for instance, an expression for the energy of the ground state of the operator H_0:

$$E = -\frac{3}{8\pi i}\int_C \frac{ds}{\sqrt{s}} \ln D(s) + 2\sum_k V_k f_k + \sum_k f_k^2, \tag{1.16}$$

where according to (1.15)

$$D(s) = 1 - \frac{2}{3(2\pi)^3}\int \frac{k^2 f_k^2 \omega_k}{s - \omega_k^2}\, d\mathrm{k}. \tag{1.17}$$

If we moreover denote by α_k the physical-particle operators in terms of which $\mathcal{H}_0$ is a diagonal operator, we can show that[7]

$$[a_k, a_{k'}^+] = [\alpha_k, \alpha_{k'}^+] = \delta_{kk'}, \qquad [H_0, \alpha_k^+] = \omega_k \alpha_k^+ \tag{1.18}$$

and that the mathematical expectation of H_1 with respect to the eigenfunctions Λ of the operator H_0 is equal to zero. The operators a_k are linear combinations of the operators α_k of the physical particles*

$$a_k = (M_+)_{kk'}\alpha_{k'} + (M_-^*)_{kk'}\alpha_{k'}^+, \quad a_k^+ = (M_+^*)_{kk'}\alpha_{k'}^+ + (M_-)_{kk'}\alpha_{k'}, \tag{1.19}$$

where the matrices M_+ and M_- are of the form

$$(M_\pm)_{kk'} = \tfrac{1}{2}(\omega_k\omega_{k'})^{-1/2}(\omega_k \pm \omega_{k'})(k\,|\,\Omega_+\,|\,k'),$$
$$(k\,|\,\Omega_\pm\,|\,k') = \delta(k - k') + \mathbf{k}\mathbf{k}' f_k f_{k'} \frac{2(\omega_k\omega_{k'})^{1/2}}{(\omega_{k'}^2 - \omega_k^2 \pm i\varepsilon)\, D_\pm(\omega_k^2)}. \tag{1.20}$$

The ground state functional Λ_0 satisfies the equation $\alpha_k\Lambda_0 = 0$, and from this it follows that Λ_0 is of the form

$$\Lambda_0 = \mathrm{const}\cdot\exp\left\{\frac{1}{2}\iint a_k^+ A_{kk'} a_{k'}^+\, dk\, dk'\right\}\Phi_0;$$
$$A^* = M_- M_+^{-1}, \quad a_k\Phi_0 = 0. \tag{1.21}$$

The polaron state eigenfunction can thus be approximately written in the form

$$\Psi_0 = \exp\left\{i\left(\mathbf{P} - \sum_k \mathbf{k} a_k^+ a_k\right)\mathbf{r}\right\}\exp\left\{\sum_k f_k(a_k - a_k^+)\right\}\cdot\Lambda_0. \tag{1.22}$$

We now determine the form of the function f_k from the condition that the energy (1.16) be a minimum. Setting the functional derivative of E with respect to f_k equal to zero we get for f_k the integral equation

$$f_k = -V_k/(1 + k^2/2\mu), \tag{1.23}$$
$$\mu^{-1} = \frac{\omega_k}{2\pi i}\int_C \frac{ds}{\sqrt{s}}\frac{1}{(s - \omega_k^2)\, D(s)}. \tag{1.24}$$

The method of solving the problem by perturbation theory is evident. It consists in expanding in (1.24) the function $D^{-1}(s)$ in a power series and integrating afterwards over s. We give here the expressions obtained in that way for the self-energy and for the polaron effective mass:

$$E = -g^2 - 1.26(g^2/10)^2 - 1.875(g^2/10)^3,$$
$$m^* = 1 + g^2/6 + 2.24(g^2/10)^2. \tag{1.25}$$

The result (1.25) for E is somewhat better than the one from the path integral method.[8] The operator gives a contribution only to the term in g^6.

2. THE STRONG-COUPLING REGION

We turn now to the main problem, the strong-coupling approximation. To elucidate the character of the solution in that region we turn to the analytical properties of the function D(s). To do this we write the function D(s) in the form

$$D(s) = D(1) + \frac{s-1}{3\pi^2}\int_0^\infty \frac{k^4 f_k^2 \omega_k\, dk}{(\omega_k^2 - 1)(\omega_k^2 - s)}, \tag{2.1}$$

where D(1) is the value of D(s) at s = 1:

$$D(1) = 1 + Q \equiv 1 + \frac{1}{3\pi^2}\int_0^\infty \frac{k^4 f_k^2 \omega_k}{\omega_k^2 - 1}\, dk. \tag{2.2}$$

As a function of the complex variable s, D(s) possesses the following properties: 1) D(s) has a cut along the real axis from s = 1 to ∞ and has not other singularities; 2) $D^*(s) = D(s^*)$; 3) as $s \to \infty$, sD(s) increases at least as s. Because of these properties we can write for $[(s-1)D(s)]^{-1}$

$$\frac{1}{(s-1)D(s)} = \frac{1}{2\pi i}\int_{C+\rho} \frac{ds'}{(s'-s)(s'-1)D(s')}, \tag{2.3}$$

where $C + \rho$ is the contour of Fig. 2.

It follows from (2.3) that $D^{-1}(s)$ satisfies the integral equation

$$\frac{1}{D(s)} = \frac{1}{1+Q} + \frac{s-1}{3\pi^2}\int_0^\infty \frac{k^4 f_k^2 \omega_k\, dk}{(s - \omega_k^2)(\omega_k^2 - 1)\,|D(\omega_k^2)|^2}. \tag{2.4}$$

Integrating by parts we can write Eq. (1.12) for ΔE in the form

$$\Delta E = \frac{1}{2\pi^2}\int_0^\infty dk k^4 f_k^2 \omega_k \frac{1}{2\pi i}\int_C \frac{\sqrt{s}}{(s - \omega_k^2)^2}\frac{1}{D(s)}\, ds,$$

and using this and (2.4) we get

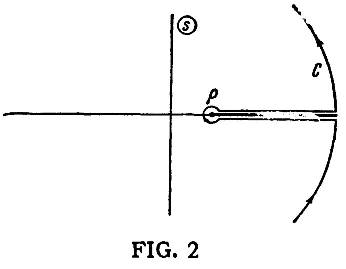

FIG. 2

---

*We sum (integrate) over repeated indices.

$$\Delta E = \frac{1}{2\pi^2}\int_0^\infty \frac{k^4 f_k^2 dk}{2(1+Q)} + \frac{1}{12\pi^4}\iint_0^\infty \frac{k^4 f_k^2 p^4 f_p^2 \omega_p \{\omega_k\omega_p + \omega_k(\omega_k+\omega_p)+1\}}{(\omega_k+\omega_p)^2(\omega_p^2-1)\,|\,D(\omega_p^2)\,|^2}\,dpdk. \tag{2.5}$$

Using (2.4) we can write Eq. (1.24) for μ^{-1} in the form

$$\mu^{-1} = \frac{1}{1+Q} + \frac{1}{3\pi^2}\int_0^\infty \frac{p^4 f_p^2(\omega_k\omega_p+1)\,dp}{(\omega_p^2-1)(\omega_k+\omega_p)\,|\,D(\omega_p^2)\,|^2}. \tag{2.6}$$

The constant Q introduced in Eq. (2.2) above is connected with the renormalization of the charge in the following way. Had we written the expression for the energy operator $\mathscr{H}_0$ in the form

$$\mathscr{H}_0 = \sum_k \omega_k a_k^+ a_k + \lambda\Big(\sum_k \mathbf{k} f_k (a_k + a_k^+)\Big)^2,$$

the renormalized coupling constant $\bar{\lambda}$ would be determined, as in ordinary pair meson theory,[9] from the relation

$$\bar{\lambda} = \lambda/(1+\lambda Q). \tag{2.7}$$

Equation (2.6) is in the general case very complicated and its exact solution almost impossible. We therefore evaluate the energy by a direct variational principle, and put the function f_k equal to

$$f_k = -V_k \exp(-k^2/2a^2), \tag{2.8}$$

where a is a parameter to be varied, and where one can easily check that for strong coupling $a^2 \gg 1$. Substituting (2.8) into (1.17) we find for the real and imaginary parts of D(s) the expressions

$$\mathrm{Re}\,D(\omega_k^2) = 1 + \lambda v(y), \qquad \mathrm{Im}\,D(\omega_k^2) = k^3 f_k^2/6\pi;$$

$$v(y) = 1 - ye^{-y^2}\int_0^y e^{t^2}dt - \xi e^{\xi^2}\int_\xi^\infty e^{-t^2}dt;$$

$$\lambda = 4g^2 a/3\sqrt{2\pi}, \qquad y = k/a, \qquad \xi = \sqrt{y^2 + 4/a^2}. \tag{2.9}$$

In the strong coupling region $\xi \to y$, and the expression for the energy E can, if we use (1.16) and (2.5), be written in the form

$$E = \frac{3}{16}a^2\left[1 + q\left(\frac{1}{\lambda}\right)\right] - \frac{g^2 a}{\sqrt{\pi}}\left(2 - \frac{1}{\sqrt{2}}\right); \tag{2.11}$$

$$q\left(\frac{1}{\lambda}\right) = \frac{2}{\sqrt{\pi}}\int_0^\infty \frac{e^{-y^2}(1-\Omega(y))\,dy}{(1/\lambda + v(y))^2 + \pi y^2 e^{-2y^2}/4},$$

$$\Omega(y) = 2y^2\left\{(1+2y^2)\,ye^{y^2}\int_y^\infty e^{-t^2}dt - y^2\right\}. \tag{2.12}$$

In the strong coupling region we put $1/\lambda \to 0$. As a result of numerical integration we obtained for q(0) the value q(0) = 5.75,[*] and from this we get by varying E with respect to a

$$E = -0.105g^4. \tag{2.13}$$

This energy value is very close to the well-known result $E = -0.106\,g^4$.[8,10] The effective Hamiltonian H_0 chosen earlier thus already contains in it the usual strong coupling approximation.

An electron in the conduction band causes polarization of the ionic lattice. This polarization is characterized by the density of the continuously distributed charge $\rho(|\mathbf{r}-\mathbf{r}_e|)$, which can be evaluated from the usual equations $(\zeta = |\mathbf{r}-\mathbf{r}_e|)$

$$4\pi\rho(\zeta) = -\nabla^2\varphi(\zeta), \tag{2.14}$$

$$\varphi(\zeta) = -\frac{1}{e}\Big(\Psi(r_e), \sum_k V_k (a_k e^{i\mathbf{kr}} + a_k^+ e^{-i\mathbf{kr}})\,\Psi(r_e)\Big). \tag{2.15}$$

Substituting into (2.15) the functionals (1.22) found earlier we get, using the fact that $(\Lambda_0, a\Lambda_0) = 0$, the following expression for ρ:

$$\rho(\zeta) = -e^2\left(\frac{1}{n^2} - \frac{1}{\varepsilon}\right)\frac{a^3}{(2\pi)^{3/2}}e^{-\zeta^2 a^2/2}. \tag{2.16}$$

The total induced charge e' is equal to

$$e' = -e\left(\frac{1}{n^2} - \frac{1}{\varepsilon}\right). \tag{2.17}$$

If we define arbitrarily the polaron radius r_p as the radius of the sphere inside of which there is half of the induced charge (2.17), we get for r_p the expression[†]

$$r_p = \frac{2.18}{a}\left(\frac{\hbar}{2m\omega}\right)^{1/2}. \tag{2.18}$$

3. POLARON SCATTERING. THE MAXIMUM VALUE OF THE COUPLING CONSTANT

One must construct the theory of scattering of polarons by optical lattice vibrations as a resonance scattering theory, as was shown convincingly by Schultz.[3] In the weak-coupling region the theory leads to the same results for the mobility as the usual consideration, that is, it leads to the equations of Fröhlich, Mott, and Davydov and Shmushkevich.[11]

To calculate the scattering amplitude we use Low's well-known method.[4] According to Low

---

[*] It is of interest to note that as $\lambda \to \infty$ the integrand in (2.12) has a steep maximum at $y^4 = 3\lambda/4$; however, if we take into account that the domain of integration over y is in fact limited and if we use the values $g^2 \approx 10$ considered in the following, this singularity does not arise.

[†] We must note that the integration in all formulae is over the dimensionless parameter $k\,(\hbar/m\omega)^{1/2}$. We have written Eq. (2.18) for clarity in the original system of units [see (1.2) and (1.3)].

we can write the required matrix element of the scattering matrix S in the form ($\hbar = 1$)

$$\langle \mathbf{P}, \mathbf{k} | S - 1 | \mathbf{P}_0, \mathbf{k}_0 \rangle = -2\pi i \delta (E - E_0) R; \tag{3.1}$$

$$R = V_{k_0} V_k \int dv \{(\Psi, e^{-i\mathbf{kr}} (H - E - \omega^0 - i\varepsilon)^{-1} e^{i\mathbf{k}_0\mathbf{r}} \Psi_0)$$
$$+ (\Psi, e^{i\mathbf{k}_0\mathbf{r}} (H - E + \omega^0 - i\varepsilon)^{-1} e^{-i\mathbf{kr}} \Psi_0)\}. \tag{3.2}$$

The initial momenta of the polaron and of the phonon are respectively denoted by $\mathbf{P}_0$ and $\mathbf{k}_0$, and the final momenta by $\mathbf{P}$ and $\mathbf{k}$; $E = P^2/2m^*$ is the polaron energy, and Ψ_0 and Ψ are the wave functionals (1.22) of the initial and final polaron states.

In the following we consider the low temperature region where $P^2/2m^* < \omega^0$. The only term responsible for scattering will in this case be the first term in (3.2) which can be evaluated as follows. We push consecutively the operators $\exp\{i(\mathbf{P}_0 + \mathbf{k}_0 - \Sigma_k \mathbf{k} a_k^+ a_k)\mathbf{r}\}$ and $\exp\{\Sigma_k f_k (a_k - a_k^+)\}$ through $(H - E - \omega^0 - i\epsilon)^{-1}$ from the right to the left and integrate the expression obtained in this way over the volume dv. We get as a result

$$\langle \mathbf{P}, \mathbf{k} | S - 1 | \mathbf{P}_0, \mathbf{k}_0 \rangle$$
$$= -i (2\pi)^4 \delta (E - E_0) \delta (\mathbf{P}_0 + \mathbf{k}_0 - \mathbf{P} - \mathbf{k}) M. \tag{3.3}$$

Here

$$M = V_k V_{k_0} (\Lambda_0, (H_0' + H_{\mathrm{I}}' - \omega^0 - i\varepsilon)^{-1} \Lambda_0),$$

$$H_0' = H_0 + \mathbf{Pk}/\mu + k_0^2/2m,$$

$$H_{\mathrm{I}}' = H_{\mathrm{I}} - \frac{1}{m} \sum_k \mathbf{kk}_0 a_k^+ a_k - \frac{1}{m} \sum_k \mathbf{kk}_0 f_k (a_k + a_k^+);$$

$$\mu \equiv m (1 - \eta)^{-1}, \quad \eta \mathbf{P} \equiv \sum_k \mathbf{k} f_k^2; \tag{3.4}$$

H_0 and H_1 are given by (1.9) and (1.10).

To evaluate (3.3) we follow Low and Pines[2] and introduce a functional Ω:

$$c\Omega = (H_0' + H_{\mathrm{I}}' - E - \omega^0 - i\varepsilon)^{-1} \Lambda_0, \tag{3.5}$$

$$c = (k_0^2/2m + \mathbf{P}_0 \mathbf{k}_0/\mu - \omega^0 - i\varepsilon)^{-1}, \tag{3.6}$$

which satisfies the integral equation

$$\Omega = \Lambda_0 - (H_0' - E - \omega^0 - i\varepsilon)^{-1} H_{\mathrm{I}}' \Omega. \tag{3.7}$$

We write Ω in the form

$$\Omega = u\Lambda_0 + \sum_k v_k a_k^+ \Lambda_0 + \sum_{k,k'} W_{kk'} a_k^+ a_{k'}^+ \Lambda_0 + \ldots \tag{3.8}$$

In the single-phonon approximation, $\Omega = u\Lambda_0 + \Sigma_k v_k a_k^+ \Lambda_0$, we get for the coefficients u and v_k the following set of equations:

$$u = 1 - c \sum_k v_k \varphi_k, \tag{3.9a}$$

$$\delta E_k v_k = -u\varphi_k - u \sum_{k'} A_{kk'} \varphi_{k'} - \frac{u}{m} \sum_{k'} \mathbf{kk}' f_{k'} A_{kk'}$$
$$- \frac{1}{m} \sum_{k'} \mathbf{kk}' f_k f_{k'} v_{k'} - \frac{1}{m} \sum_{k'k''} A_{kk'} f_{k'} \mathbf{k}'\mathbf{k}'' f_{k''} v_{k''}, \tag{3.9b}$$

where

$$\delta E_k = (\mathbf{k}_0 - \mathbf{k})^2/2m + \mu^{-1} \mathbf{P}_0 (\mathbf{k}_0 - \mathbf{k}) - i\varepsilon,$$

$$\varphi_k = -\mathbf{kk}_0 f_k/m + V_k + f_k \omega_k = -\mathbf{kk}_0 f_k/m + \Phi_k. \tag{3.10}$$

If we recognize that (1.20) and (1.21) imply that the matrix $A_{kk'}$ can be written as $A_{kk'} = (\mathbf{k}\cdot\mathbf{k}')Q(k, k')$, the solution of these equations can be written in the form

$$cu = \left\{\frac{k_0^2}{2m} \frac{1 - I - K + 2U}{1 + I + K} - \omega^0 (N + T + 1)\right\}^{-1};$$
$$U = 2L + M + (L + S)(L + M), \tag{3.11}$$

$$I = \sum_k \frac{(\mathbf{kk}_0)^2 f_k^2}{m k_0^2 \delta E_k}, \quad K = \sum_k \frac{(\mathbf{kk}_0)^2 f_k T_k}{m k_0^2 \delta E_k}, \quad L = \sum_k \frac{\mathbf{kk}_0 f_k \Phi_k}{k_0^2 \delta E_k},$$

$$M = \sum_k \frac{\mathbf{kk}_0 \Phi_k T_k}{k_0^2 \delta E_k}, \quad S = \sum_k \frac{\mathbf{kk}_0 k^2 f_k T_k}{m k_0^2 \delta E_k}, \quad T = \frac{1}{\omega^0} \sum_k \frac{k^2 f_k \Phi_k}{m \delta E_k},$$

$$N = \frac{1}{\omega^0} \sum_k \frac{\Phi_k^2}{\delta E_k}, \quad T_k \equiv \sum_{k'} \frac{(\mathbf{kk}')^2}{k'^2} Q(k, k'). \tag{3.12}$$

After integrating over the final momenta P and k and over the initial momentum k_0 we get for the probability w for scattering per unit time the following expression

$$w = \frac{1}{\tau} = \frac{m^* P_0}{8\pi^4} \int |V_{k_0}|^4 |cu(k_0)|^2 e^{-\omega_0/kT} dk_0. \tag{3.13}$$

The factor $\exp(-\omega^0/kT)$ gives the number of phonons per unit volume at low T as a function of the temperature T. The function $|cu(k_0)|^2$ is of the form

$$|cu(k_0)|^2 = 1/(A^2 + P_0^2 B^2) \tag{3.14}$$

and as $P_0 \to 0$ the integrand in (3.13) has thus the form

$$\lim_{P_0 \to 0} \frac{P_0}{A^2 + P_0^2 B^2} = \frac{\pi}{B} \delta(A),$$

that is, the scattering cross section is determined by the magnitude of the resonance momentum $A(k_r) = 0$. When $g^2 \approx 1$, Eq. (3.13) becomes Low and Pines' well-known formula.[2]

When the coupling constant increases the magnitude of the resonance momentum will increase also, and in the strong coupling case the integrals (3.12) can thus be evaluated in the limit of large k_0. In that region the quantities L, M, S, and T are of order g^{-4} compared to the main terms I and N, and the integral K turns out on an estimate to be approximately an order of magnitude smaller than I. In the strong coupling region we get for the resonance momentum, after evaluating the integrals I and N in (3.11), the expression

$$\frac{k_r}{\sqrt{2m\omega^0}} = a\left(\frac{g^2 a}{6\sqrt{2\pi}}\right)^{1/2}\left(1+\frac{27}{8}\frac{\sqrt{2\pi}}{g^2 a}+O(g^{-6})\right). \quad (3.15)$$

We now consider the contribution from the two-phonon terms to the scattering amplitude. If we retain in the expansion (3.8) the terms $\Sigma_{kk'} W_{kk'} a_k^+ a_{k'}^+ \Lambda_0$ the equation for the coefficients $W_{kk'}$ becomes

$$\left\{\omega^0 + \frac{(\mathbf{k}+\mathbf{k}'-\mathbf{k}_0)^2}{2m}\right\} W_{kk'} = -\frac{u}{2m}\{(\mathbf{k}+\mathbf{k}')\mathbf{k}_0 - (\mathbf{kk}')\} A_{kk'}$$
$$-\frac{\mathbf{kk}'}{2m}(v_k f_{k'} + v_{k'} f_k) - \frac{1}{2}(v_k \varphi_{k'} + v_{k'} \varphi_k)$$
$$+ \text{ integral terms.} \quad (3.16)$$

The left-hand side of (3.16) contains the parameter k_0 squared, and the right-hand side only to the first power. If we take this into account, the correction terms in $W_{kk'}$ in Eq. (3.9b) for v_k will be of the order $k_0^{-1} \sim g^{-4}$ as compared with the terms written down in (3.9b). In the strong coupling region the two-phonon terms thus make a small contribution to the scattering amplitude.

Let us dwell on the problem of the maximum values of the coupling constant g of the electron-phonon interaction. The maximum value of the phonon quasi-momentum is $k_{max} = 2\pi/a^0$, where a^0 is the lattice constant. Since the right-hand side of Eq. (3.15) increases as g^4 in the strong coupling region, we can find such values of g that the scattering cannot take place at all, for when the coupling constant increases the lattice vibrations with the very shortest wavelengths become responsible for the scattering.

The maximum momentum corresponds to a wavelength $\lambda = a^0$. In that wave all ions in the lattice are at the nodes of the wave; it hardly makes sense therefore to speak of scattering by this wave, which is in actual fact a fictitious one. Even if we make the extreme assumption that all of the mobility of the polarons is caused only by the scattering by a single wave with $k = \pi/a^0$, which is already connected with a displacement of the ions, this assumption will lead to a rather severe limitation on the coupling constant. These values were evaluated using (3.15) and are listed in the table.

For most polar crystals the values of g^2_{max} are thus of the order of 8 or 9. These values actually reduce to zero the region where the strong coupling can be applied, i.e., weak or intermediate coupling must occur in real crystals. The most important consequence following from this is the relatively small magnitude of the polaron effective mass. Indeed, even if we make the extreme non-physical assumption that all of the mobility is connected with the scattering by the shortest wavelength in the crystal, we get an appreciable error in the result obtained from the asymptotic formula for the polaron effective mass, $m^*/m = 0.020 g^8$ [8] for $g^2 \approx 8$ to 9 (in contradistinction to the energy): [3] for instance, if $g^2 \leq 8$, the effective mass must be less than 30 m.

The restrictions on the permissible coupling-constant values follow, of course, also from the condition that the polaron dimensions must not be less than the lattice constant. This criterion leads, however, to values of g^2 larger than the ones in the table and, moreover, this criterion is not so well defined as the one we just considered which is based upon scattering theory.

Let us consider some other observations about the theory. In all preceding calculations we assumed that the upper limit of integration could be taken to be infinite. In the weak or intermediate coupling regions this assumption is undoubtedly correct since the integrands decrease steeply with increasing k, but in the strong coupling region this problem requires a more detailed consideration. We already mentioned that the integration

Crystal	a^0, Å	$\hbar\omega\cdot 10^2$, ev	$\frac{2\pi}{a^0}\left(\frac{2\hbar}{2m\omega^0}\right)^{-1/2}$	g_0^2	g_{max}^2
LiF	4.02	8.37	10.6	5,2	7,7
NaF	4.62	5,68	11.2	6.3	8.6
NaCl	5,63	3.21	12.1	5.5	8,4
NaBr	5.96	2,51	12.8	5.0	8.3
NaJ	6.46	2,19	12.8	4.8	8.1
KCl	6.28	2.61	12.1	5.8	8.6
KBr	6,58	2.01	13.1	5.7	8,8
KJ	7.05	1.65	13.5	4.9	8.4
RbCl	6.54	2.21	12,6	6.4	9.1
RbBr	6.85	1.60	14,2	6,7	9.7
RbJ	7,33	1.33	14.5	5.8	9.2
AgCl	5.54	2,41	14.2	3.9	7.8

over k means an integration over the dimensionless parameter $k(\hbar/m\omega^0)^{1/2}$. It is clear from the table that we can on an average put $k_{max}(\hbar/2m_0\omega^0)^{1/2} \approx 12$, and we then get for the typical case when $g_0^2 = 5$

$$x_{max} = k_{max}(\hbar/m\omega^0)^{1/2} \approx 60\sqrt{2}/g^2.$$

When evaluating the integrals in (2.12) and (2.13) we made the change of variable $y = x/a$ and set the upper limit of integration for $g^2 \approx 9$ at about $y = 3.66$. The numerical integration in (2.12) was taken up to 3.5, beyond which the integrand was vanishingly small. One can thus assume that the numerical value for the energy given here is basically correct.

Considering the strong coupling region further, we must show the extent to which the operator H_1 is a perturbation with respect to H_0. If we use perturbation theory to evaluate the contribution from H_1 to the energy, we can, owing to the fast decrease of the function f_k at large k, make the numerical contribution from H_1 small in the range of g^2 values considered above. At any rate, taking the operator H_1 into account leads to a decrease in the energy, as compared with (2.13), and to a smaller polaron radius. The values of g_{max}^2 given in the table are therefore still undoubtedly overestimates.

It follows from all this that strong coupling turns out to be in fact incompatible with the scattering of polarons by optical lattice vibrations. Taking dispersion into account has no important influence whatever on this result since the large k region makes a small contribution to the numerical values of the integrals I and N. As far as the already well-known experimental data are concerned, they indicate either the use of weak (PbS, PbSe) or intermediate coupling (AgCl, AgBr).[12] The latter crystals are of most interest since the numerical values of the mobility enable us in that case to estimate in the most direct manner the magnitude of the polaron effect; we shall consider these problems later.

In conclusion I express my deep gratitude to Academician V. A. Fock for a number of valuable hints and also to Professor H. Lehmann and W. Zimmermann for their interest in this paper and to Professor G. Höhler for drawing my attention to Schultz's paper.[3] I am grateful to Professor L. É. Gurevich and V. I. Perel' for an interesting discussion.

---

[1] S. I. Pekar, Issledovanie po elektronnoĭ teorii kristallov (Study of the Electron Theory of Crystals), Gostekhizdat, 1951, German translation Akademie Verlag 1954.

[2] F. E. Low and D. Pines, Phys. Rev. **98**, 414 (1955).

[3] T. D. Schultz, Phys. Rev. **116**, 526 (1959); H. Osaka, Progr. Theoret. Phys. (Kyoto) **25**, 517 (1961).

[4] F. E. Low, Phys. Rev. **97**, 1392 (1955).

[5] Lee, Low, and Pines, Phys. Rev. **90**, 297 (1953).

[6] E. P. Gross, Phys. Rev. **100**, 1571 (1955).

[7] A. V. Tulub, Vestnik LGU (Leningrad State Univ.) **22**, 104 (1960).

[8] R. P. Feynman, Phys. Rev. **97**, 660 (1955).

[9] A. Klein and B. H. McCormick, Phys. Rev. **98**, 1428 (1955).

[10] V. M. Buĭmistrov and S. I. Pekar, JETP **32**, 1193 (1957), Soviet Phys. JETP **5**, 970 (1957); G. Höhler, Z. Physik **146**, 372 (1956).

[11] H. Fröhlich and N. F. Mott, Proc. Roy. Soc. (London) **A171**, 496 (1939); B. I. Davydov and I. M. Shmushkevich, UFN **24**, 21 (1940).

[12] K. Kobayashi and F. C. Brown, Phys. Rev. **113**, 507 (1959); Burnham, Brown, and Knox, Phys. Rev. **119**, 1560 (1960).

Translated by D. ter Haar
310