5.All the results enumerated above are independent in their qualitative aspects of any special choice of the potential energy U.

I take this opportunity to express my deep appreciation to K. B. Tolpygo who suggested and guided this work.

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185

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Band Structure of the Polaron Energy Spectrum

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Using the macroscopic treatment of the polaron as the zeroth approximation, the periodic potential of a crystal and the periodic variation of its polarizability with variations in the position of the polaron center of gravity are calculated in the first approximation. We determine the dependence of the energy of a crystal with a polaron on the position of the polaron's center of gravity, and it is found possible to treat polaron motion as the motion of a particle with the polaron mass M in a field with a periodic potential. We determine the widths and spacings of the lowest forbidden and allowed energy bands. A numerical calculation is performed for NaCl, KCl, KBr, and KI.

1. STATUS OF THE PROBLEM

GREAT SUCCESSES in the theory of the electric conductivity of ionic crystals were attained as a result of Pekar's polaron theory[1, 2] in which the interaction between electrons and polar vibrations of the crystal are introduced into the fundamental Hamiltonian of the problem. The periodic potential of the crystal is eliminated with the aid of the effective-mass method[3] (EMM). It is found that electron motion is composed of vibration within a polarization well and wave-like translation of the electron together with the polarization well through the crystal[4]. For a fixed crystal polarization the electron energy spectrum is found to be discrete. At the same time, the problem of electron and ion motion possesses translational degeneracy[2], so that the energy spectrum of the whole crystal is found to be continuous:

$$E = J[\psi] + (\hbar^2 K^2/2M) - {}^3/_2\,\hbar\omega + E_{\text{ion}}, \quad (1)$$

where K and M are the wave vector and effective mass of the polaron[5], $J[\psi]$ is the energy of the crystal with a stationary polaron, and ω is the limiting longitudinal optical crystal vibrations.

The translational degeneracy of the problem of polaron motion led several authors[6, 7] to assert that the electron energy spectrum should have a bandlike structure, and that therefore polaron theory is essentially band theory in which the interaction between the electron and the crystal polarizations has been accounted for. This leads only to a formal change of the specific parameters of the current carriers, and according to Tiablikov[7] is of no great consequence, since these parameters are usually obtained experimentally anyway. As was asserted by Tiablikov[8], Eq. (1) gives the energy only in the neighborhood of the lower edge of the first polaron band.

In other works[9-11], Tiablikov suggested a method for calculating the electron energy spectrum by accounting for interactions with the phonon field similarly as is done in quantum electrodynamics. According to his calculations, this spectrum consists of relatively narrow (10^2 ev) bands separated by relatively wide forbidden gaps.

These calculations, however, cannot be considered reliable, since the formulae of the last article[11] are not carried to final form, and the first two articles[9, 10] contain several defects: 1) in spite of the fact that he is treating a polaron of small radius the author makes use of the macroscopic formula for the interaction only with longitudinal optical vibrations of the lattice, and neglects frequency dispersion; 2) Tiablikov's[8] Eq. (13′), which describes electron vibrations and involves the potential $V_0(\mathbf{r})$ of a single ion rather than the periodic potential, gives an electron-state radius less than the dimensions of the ion, and a level lying at a depth of the order of the ionization potential of the hydrogen atom; in this one may not ignore the orthogonality of this wave function to the internal electron functions of the ion; 3) according to Tiablikov[8], electron motion reduces to skipping from atom to atom, and the crystal polarization occurs each time after the electron "jumps." Thus the polarization potential is actually periodic and the total polarization is non-inertial, so that the author is in fact simply considering a band electron with a different effective mass. Thus the conclusion on the existence of polaron bands is contained in the original assumptions of Tiablikov's work, and according to the above, the numerical calculations may give results which differ significantly from actual values.

Furthermore, it is impossible to agree with Vol'kenshtein and Tiablikov when they state that Pekar obtained a continuous polaron spectrum as a result of an inconsistent treatment of translational degeneracy [the wave function of the polaron is not of the form $e^{i\mathbf{K}\mathbf{r}}u_{\mathbf{K}}(\mathbf{r})$] and the application of the EMM.

As has been shown by Pekar[2], the Hamiltonian of an electron in an inertially polarizable crystal is invariant with respect to simultaneous translation of the electron and polarization of the crystal along an arbitrary vector ξ. The wave function of the polaron is not an eigenfunction of the translation operator, but is a linear combination of such eigenfunctions belonging to the same energy level. It is therefore an eigenfunction of the energy operator. By a special choice of variables one may easily obtain an eigenfunction of the translation operator which has the same characteristics as Pekar's function. In this case, however, the mass and mobility of the polaron will be exactly the same as that given by Pekar. Elsewhere[12] Pekar has shown by several examples that the fact of translational symmetry alone does not lead to a band spectrum.

As for the use of the EMM, it is well known that its accuracy increases when $r_p \gg a$, where r_p is the polarization radius of the polaron, and a is the separation between closest ions. As has been shown by one of the present authors[13], when r_p is of the order of several times a, the error in the EMM is insignificant, so that in dealing with a polaron of energy spectrum is by no means only of academic interest, and it is far from sufficient to answer it affirmatively "in principle" and leave the determination of the specific current carrier parameters to the experimentalists. For certain definite relations between the forbidden and allowed bandwidths and the magnitude of kT, qualitatively new effects may take place. If a suitable quantitative theory were to predict such relations, it could provide direction also for experimental work.

The present work, to our knowledge, is the first attempt to perform a quantitative calculation of the lowest polaron bands.

2. METHOD OF APPROXIMATION

In view of the great complexity of the general problem, we consider relatively slow motion of the polaron, when we can neglect energy transfer to the crystal[14]. In addition, we assume that the polaron radius is large enough ($r_p \gg a$) for the results of Pekar's macroscopic theory[2] to be treated as the zeroth approximation. The consideration of even a stationary polaron of small radius is an independent and quite difficult problem.

The reason that the polaron spectrum is continuous in Pekar's theory lies in the fact that the energy $J[\psi]$ of the crystal with an electron is independent of the coordinate ξ of the polaron center of gravity. As a result, the equation for the translational motion of the polaron[2]

$$-(\hbar^2/2M)\,\nabla_\xi^2\Psi + J[\psi]\,\Psi = E\Psi \qquad (2)$$

has plane-wave solutions $\psi = e^{i\mathbf{K}\xi}$ with energy given by Eq. (1).

Strictly speaking, the functional $J[\psi]$ which determines the electron energy in the first stage of the adiabatic approximation for the equilibrium positions of the ions should depend on the coordinate ξ of the polaron center of gravity: $J[\psi] = J(\xi)$.

The quantity $J(\xi)$ has the periodicity of the lattice, and therefore Eq. (2) has solutions in the form of the Bloch function

$$\psi = e^{i\mathbf{K}\xi} u_{\mathbf{K}}(\xi); \quad E = E(\mathbf{K}). \tag{3}$$

Our problem reduces to finding an explicit expression for $J(\xi)$ and integration of Eq. (2). This expression depends on the discrete crystal structure, which must therefore be borne in mind. In calculating the energy in the first approximation, we may use the wave function of the zeroth approximation which is obtained with the aid of the EEM, in which the crystal is treated as a continuum.

Let the Schroedinger equation for the polaron

$$[-(\hbar^2/2m)\Delta + V_p(\mathbf{r}) + W(\mathbf{r})]\,\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{4}$$

have the zeroth approximation solution

$$\psi = \sum_{\mathbf{K}} a_{\mathbf{K}}\, \psi_{\mathbf{K}}(\mathbf{r}) = \sum_{\mathbf{K}} a_{\mathbf{K}}\, e^{i\mathbf{K}\mathbf{r}} u_{\mathbf{K}}(\mathbf{r}), \tag{5}$$

where $\psi_{\mathbf{K}}(\mathbf{r})$ are Bloch functions, $a_{\mathbf{K}}$ are the Fourier coefficients of the function $\phi(\mathbf{r})$ which satisfies the equation

$$[-(\hbar^2/2\mu)\Delta + W]\,\varphi = E\varphi, \tag{6}$$

$$\varphi = V^{-1/2} \sum_{\mathbf{K}} a_{\mathbf{K}} e^{i\mathbf{K}\mathbf{r}}, \tag{7}$$

μ is the effective mass of the electron in the conduction band[3], V is the volume of the fundamental region of the crystal, and $W(\mathbf{r})$ is the polarization potential calculated in the macroscopic theory[1] using the "smoothed out" functions $\phi(\mathbf{r})$ of Eq. (7):

$$W \to \widetilde{W}(\mathbf{r}) = -e^2 \int \frac{\operatorname{div} \boldsymbol{P}(\mathbf{r}')\, d\tau'}{|\mathbf{r}-\mathbf{r}'|} = -e^2 C \int \frac{|\varphi(\mathbf{r}')|^2\, d\tau'}{|\mathbf{r}-\mathbf{r}'|}. \tag{8}$$

In the first approximation we obtain the energy by multiplying Eq. (4) by $\psi^*(\mathbf{r})$ and integrating over V,

$$E = \sum_{\mathbf{K}',\mathbf{K}} a^*_{\mathbf{K}'} a_{\mathbf{K}} \int \psi^*_{\mathbf{K}'} \Big(-\frac{\hbar^2}{2m}\Delta + V_p + W\Big) \psi_{\mathbf{K}}\, d\tau = \sum_{\mathbf{K}} |a_{\mathbf{K}}|^2 E(\mathbf{K}) + \sum_{\mathbf{K},\mathbf{K}'} a^*_{\mathbf{K}'} a_{\mathbf{K}} \int \psi^*_{\mathbf{K}'} W \psi_{\mathbf{K}}\, d\tau, \tag{9}$$

where $E(\mathbf{K})$ is the energy of a band electron in the state $\psi_{\mathbf{K}}$.

Let $\phi^0(\mathbf{r})$ be the smoothed out function for a polaron at rest at the origin, and $a^0_{\mathbf{K}}$ be its expansion coefficients. Then the solution of Eq. (6) for a polaron whose center is at ξ will be, taking account of Eq. (8),

$$\varphi(\mathbf{r}) = \varphi^0(\mathbf{r} - \xi) : a_{\mathbf{K}} = a^0_{\mathbf{K}} e^{-i\mathbf{K}\xi}. \tag{10}$$

The first term of Eq. (9) is independent of ξ, and the ξ-dependence of the second term is lost in the macroscopic theory (without any significant error in the absolute magnitude of the energy[13, 15], since when calculating the integral

$$\int \psi^*_{\mathbf{K}'} W \psi_{\mathbf{K}}\, d\tau = \int e^{i(\mathbf{K}-\mathbf{K}')\mathbf{r}} W u^*_{\mathbf{K}'} u_{\mathbf{K}}\, d\tau$$

the rapidly oscillating factor $u^*_{\mathbf{K}'} u_{\mathbf{K}}$ was taken outside the integral sign and its average value, about equal to unity, was used, and W was replaced by $\widetilde{W}$ of Eq. (8).

We shall calculate E from Eq. (9) using the detailed polaron function $\psi_{\mathbf{K}}(\mathbf{r})$ given by Eq. (5) instead of the smoothed out function, and shall account for the discrete structure of the crystal in finding the mean polarization energy W. To do this one must specify the form of the Bloch functions $\psi_{\mathbf{K}}(\mathbf{r})$. For reasons given elsewhere[13], we shall make use of the approximation of strongly bound electrons and assume that for energies that are not very large the electron moves only on positive ions of the lattice:

$$\psi_{\mathbf{K}}(\mathbf{r}) = N^{-1/2} \sum_{l} \psi_a(\mathbf{r} - \mathbf{r}^l_1) \exp(i\mathbf{K}\mathbf{r}^l_1), \tag{11}$$

where ψ_a is the atomic function of a valence electron on the positive site $\mathbf{r}^l_1$, l is the number of the cell, and N is the number of cells in the fundamental region.

We shall write $\pi^l_s = \mathbf{p}^l_s + \widetilde{\mathbf{P}}^l_s$ for the inertial dipole arising at site $\mathbf{r}^l_s$ under the action of the polaron field, and due both to the displacement $\mathbf{p}^l_s$ of the ions, and to the deformation $\mathbf{P}^l_s$ of these ions;[16, 17];

$$\mathbf{D}(\mathbf{r}^l_s) = \int \frac{(\mathbf{r}^l_s - \mathbf{r}')}{|\mathbf{r}^l_s - \mathbf{r}'|^3} |\psi(\mathbf{r}')|^2\, d\tau'$$

shall be used to denote the induction at the site $\mathbf{r}^l_s$ due to the polaron. Then the mean potential energy of the electron is

$$\overline{W} = -\sum_{sl}\pi_s^l \mathbf{D}(\mathbf{r}_s^l) = -N\sum_{s,\varkappa}\pi_{s\varkappa}\mathbf{D}_{s-\varkappa}, \tag{12}$$

where $\pi_{s\varkappa}$ and $\mathbf{D}_{s\varkappa}$ are the Fourier expansion coefficients of π_s^l and $\mathbf{D}(\mathbf{r}_s^l)$,

$$\pi_s^l = \sum_{\varkappa}\pi_{s\varkappa}\exp(i\varkappa\mathbf{r}_s^l),\ \mathbf{D}(\mathbf{r}_s^l) = \sum_{\varkappa}\mathbf{D}_{s\varkappa}\exp(i\varkappa\mathbf{r}_s^l). \tag{13}$$

Detailed analysis of the natural vibration spectra of binary crystals[16, 17] shows that all natural vibrations have some dipole moment, but that for a large-radius polaron, interacting primarily with the longitudinal optical mode, the fundamental contributions to $\pi_{s\varkappa}$ come from this mode. As has been shown elsewhere[17], in the zeroth approximation (long waves) each normal vibration of this mode has a dipole moment given by

$$\pi_{s\varkappa}^{(1)} = (\varkappa/|\varkappa|)(1/\mu_s + c_s/a_0)$$

(see Tolpygo's[17] Equation (21) and Table II, where the values of the parameters $\mu_s c_s$ and a_0 are given). The magnitude of the dipole moment $\pi_{s\varkappa}$ due to the field $\mathbf{D}_{s\varkappa}$ can be found by considering the equations for the normal coordinate $q_{1\varkappa}$ introduced by the equation $\pi_{s\varkappa} = \pi_{s\varkappa}^{(1)} q_{1\varkappa}$:

$$\ddot{q}_{1\varkappa} + \omega_{1\varkappa}^2 q_{1\varkappa} = (e_s^2/\mu)\,O_{1\varkappa}, \tag{14}$$

where e_s is the charge of the s-th ion, and μ is the reduced mass of a pair of ions.

The generalized force[14, 18] $Q_{1\varkappa}$ is $\sum_s \mathbf{D}_{s\varkappa}\pi_{s-\varkappa}^{(1)}$. Thus, in a quasi-stationary external field

$$\pi_{s\varkappa} = (\pi_{s\varkappa}^{(1)}/\omega_{1\varkappa}^2)\sum_{s'}\pi_{s'-\varkappa}^{(1)}\mathbf{D}_{s'\varkappa}. \tag{15}$$

According to Eq. (12) the mean potential energy, of the electron will be

$$\overline{W} = -N\sum_{s\varkappa}\frac{e_s^2}{\mu\omega_{1\varkappa}^2}\mathbf{D}_{s-\varkappa}\pi_{s\varkappa}^{(1)}\sum_{s'}\pi_{s'-\varkappa}^{(1)}\mathbf{D}_{s'\varkappa}, \tag{16}$$

and the potential energy of the deformed crystal[18] will be

$$U^0 = \frac{N}{2}\sum_{\varkappa}\frac{\mu}{e_s^2}q_{1\varkappa}q_{1-\varkappa}\omega_{1\varkappa}^2 = \frac{N}{.2}\sum_{\varkappa}\frac{e_s^2}{\mu}\frac{Q_{1\varkappa}}{\omega_{1\varkappa}^2}\frac{Q_{1-\varkappa}}{\omega_{1\varkappa}^2}\omega_{1\varkappa}^2 = -\frac{1}{2}\overline{W}. \tag{17}$$

In agreement with the long-wave approximation, we shall neglect dispersion and set[2] $\omega_{1\varkappa} = \omega$. Then from Eq. (9), (16), and (17) the energy of a crystal with a polaron is

$$J[\psi] = \sum_{\mathbf{K}}|a_{\mathbf{K}}|^2 E(\mathbf{K}) + \overline{W} + U^0 = \sum_{\mathbf{K}}|a_{\mathbf{K}}|^2 E(\mathbf{K}) - \frac{N}{2\omega^2}\sum_{\varkappa ss'}\frac{e_s^2}{\mu}\pi_{s\varkappa}^{(1)}\pi_{s'-\varkappa}^{(1)}\mathbf{D}_{s-\varkappa}\mathbf{D}_{s'\varkappa}. \tag{18}$$

3. THE DEPENDENCE OF THE ENERGY OF A CRYSTAL WITH A POLARON ON THE POSITION OF THE CENTER OF GRAVITY OF THE POLARON

In order to find the components $\mathbf{D}_{s\varkappa}$ of the induction, let us find the mean potential $v(\mathbf{r})$ of the ψ-shell from the equation

$$\Delta v = -4\pi e|\psi|^2 \tag{19}$$

with the ψ given by Eq. (5) and (11). Expanding the atomic functions ψ_a in a Fourier series

$$\psi_a(\mathbf{r}) = \sum_{\mathbf{K}''}\psi_{\mathbf{K}''}e^{i\mathbf{K}''\mathbf{r}},$$

we solve Eq. (19), after which we calculate $\mathbf{D}(\mathbf{r}) = -\nabla v(\mathbf{r})$ and find its Fourier coefficients. When these calculations are performed, we obtain the following expression for $J[\psi]$ of Eq. (18).

$$\begin{aligned} J[\psi] = J(\xi) = \sum_{\mathbf{K}}|a_{\mathbf{K}}|^2 E(\mathbf{K}) - \frac{8\pi^2 e^2 N^3 e_s^2}{\omega^2\mu}\sum_{ss'}\pi_{s-\varkappa}^{(1)}\pi_{s'\varkappa}^{(1)} \\ \times \sum a_{\mathbf{K}}^0 a_{\mathbf{K}'}^0 a_{\mathbf{K}-\varkappa-\mathbf{p}+\mathbf{p}'-\mathbf{p}''+\mathbf{m}}^{0*} a_{\mathbf{K}'+\varkappa+\mathbf{p}-\mathbf{p}'+\mathbf{p}''}^{0*}\psi_{\mathbf{K}+\mathbf{q}}\psi_{\mathbf{K}'+\mathbf{p}}\psi_{\mathbf{K}'+\varkappa+\mathbf{p}+\mathbf{p}''}^{*} \\ \times \psi_{\mathbf{K}-\varkappa-\mathbf{p}+\mathbf{p}'-\mathbf{p}''+\mathbf{q}'+\mathbf{m}} \times \\ \times \frac{(\mathbf{p}''+\varkappa)(\mathbf{p}''+\mathbf{p}+\mathbf{q}-\mathbf{p}'-\mathbf{q}'-\mathbf{m}+\varkappa)}{|\mathbf{p}''+\varkappa|^2|\mathbf{p}''+\mathbf{p}+\mathbf{q}-\mathbf{p}'-\mathbf{q}'-\mathbf{m}+\varkappa|^2}\exp\{i(\mathbf{q}'-\mathbf{q}+\mathbf{p}-\mathbf{p}')\mathbf{r}_1 - i\mathbf{p}''\mathbf{r}_{s'} \\ + i(\mathbf{p}''+\mathbf{q}+\mathbf{p}-\mathbf{p}'-\mathbf{q}'-\mathbf{m})\mathbf{r}_s + i\mathbf{m}\xi\}, \end{aligned} \tag{20}$$

where q, q′, p, p′, p″, and m are reciprocal lattice vectors, and the summation is taken over all indices.

Eq. (20) can be simplified: a) the EMM assumes that the $a_{\mathbf{K}}$ decrease rapidly with increasing K and only terms with $|\mathbf{K}| \ll 1/a$ are significant in Eq. (5), and b) the coefficients $\psi_{\mathbf{K}+\mathbf{q}}$ decrease rapidly with increasing q (in the examples below the decreases are as $1/q^4$ and $1/q^6$ and terms with $q = 0$ are the important ones. Therefore the main contribution to the sum in Eq. (20) is given by terms in which the indices of $a_{\mathbf{K}}$ and $\psi_{\mathbf{K}+\mathbf{q}}$ are simultaneously small, that is those terms for which $\mathbf{q} = \mathbf{p} = \mathbf{p}' = \mathbf{q}' = 0$. Of these, the largest will be those in which the product of the a coefficients is not too small. Since the main contribution comes from terms with small K, K′ and the vector $\varkappa$ is restricted by the limits of the first cell of the reciprocal lattice so that $|\varkappa| < 1/2|\mathbf{p}''|$, this product will be largest when $\mathbf{p}'' = 0$ or $\mathbf{p}'' = \mathbf{m}$. If K is replaced by K′ and $\varkappa$ by $-\varkappa$ these two terms transform into each other. The next largest terms will be those in which one of the indices of the $\psi_{\mathbf{K}}$ differs from the index of $a_{\mathbf{K}}$ by the smallest vector of the reciprocal lattice ($\psi_{\mathbf{K}}$ decreases with K less rapidly than does $a_{\mathbf{K}}$). This gives eight types of terms, and these can be transformed to four types by replacing K by K′, $\varkappa$ by $-\varkappa$, p by q, and p′ by q′:

$$1)\ \mathbf{q} \neq 0,\ \mathbf{p}'' = 0;\quad 2)\ \mathbf{q} \neq 0,\ \mathbf{p}'' = \mathbf{m};$$

$$3)\ \mathbf{q}' \neq 0,\ \mathbf{p}'' = 0;\quad 4)\ \mathbf{q}' \neq 0,\ \mathbf{p}'' = \mathbf{m}$$

(other q and p vectors are equal to 0.)

Further calculations have been performed for a lattice of the NaCl type, where

$$\mathbf{r}_1 = 0,\ \mathbf{r}_2 = a(\mathbf{i} + \mathbf{j} + \mathbf{k});$$

$$\mathbf{q}_{\min} = (\pi / a)(\pm \mathbf{i} \pm \mathbf{j} \pm \mathbf{k});$$

the sum over s, s' gives the factor $\pi_{1\varkappa}^{(1)^2} - \pi_{2\varkappa}^{(1)^2}$, in the principal term, the factor $(\pi_{1\varkappa}^{(1)} + \pi_{2\varkappa}^{(1)})^2$ in terms 1) and 3), and the factor $(\pi_{1\varkappa}^{(1)} - \pi_{2\varkappa}^{(1)})^2$ in terms 2) and 4).

4. POLARON BAND WIDTHS FOR SPECIFIC CRYSTALS

Let us take the smoothed out function $\phi(\mathbf{r})$ to be of the form

$$\varphi(\mathbf{r}) = \left(\frac{\alpha}{\sqrt{\pi}}\right)^{3/2} e^{-\alpha^2 \mathbf{r}^2/2};$$

$$a_{\mathbf{K}}^0 = 2\sqrt{\frac{2}{V}}\left(\frac{\sqrt{\pi}}{\alpha}\right)^{3/2} e^{-K^2/2\alpha^2} \tag{21}$$

and consider NaCl, KCl, KBr, KI crystals, for which the parameters of polaron theory are known. The 3s atomic functions of Na and the 4s functions of K have been approximated from the data of Fock and Petrashen'[19] and Hartree[20] by one of the authors[15] and by Dykman[21]:

$$\mathrm{Na}: \psi_a = \frac{0{,}727}{\sqrt{4\pi a_{\mathrm{b}}^3}}(1 - r/a_{\mathrm{b}}) \exp(-0{,}712\, r/a_{\mathrm{b}});$$

$$\psi_{\mathbf{K}} = \frac{0{,}727\sqrt{4\pi a_{\mathrm{b}}^3}}{V}\,\frac{2{,}31 - 3{,}42\,\mathbf{K}^2 a_{\mathrm{b}}^2}{[0{,}504 + \mathbf{K}^2 a_{\mathrm{b}}^2]^3};$$

$$\mathrm{K}: \psi_a = \frac{0{,}472}{\sqrt{4\pi a_{\mathrm{b}}^3}}(1{,}62 - r/a_{\mathrm{b}}) \exp(-0{,}569\, r/a_{\mathrm{b}}); \tag{22}$$

$$\psi_{\mathbf{K}} = \frac{0{,}944\sqrt{4\pi a_{\mathrm{b}}^3}}{V}\,\frac{1{,}922\,\mathbf{K}^2 a_{\mathrm{b}}^2 - 0{,}674}{[0{,}324 + \mathbf{K}^2 a_{\mathrm{b}}^2]^3}.$$

We may go over, in Eq. (20), from the sum over K, K′, $\varkappa$ to an integral which can be calculated approximately by finding the maximum of the product of the four $\alpha_{\mathbf{K}}$ coefficients and setting the indices K in the more smoothly varying factors $\psi_{\mathbf{K}}$ equal to their values at the maximum (for large-radius polarons this maximum is sufficiently sharp): $\mathbf{K} = -(\mathbf{m}/4) + \mathbf{K}_1$; $\mathbf{K} = -(\mathbf{m}/4) + \mathbf{K}_2$; $\varkappa = \pm[(\mathbf{m}/2) - \mathbf{K}_0]$, and $\cos(\hat{\mathbf{m}}\mathbf{K}) > 0$, since $|\varkappa| \leq |\mathbf{m}/2|$. In the principal term and in 2) and 4) we must take the minus sign, and in 1) and 3), the plus sign for $\varkappa$. Replacing q′ by −q and accounting for the dependence of $\psi_{\mathbf{K}}$ only on $|\mathbf{K}|$ [see Eq. (22)], terms 1) and 3) are joined into a single term, as are terms 2) and 4). As a result, we get the ξ-dependence of $J[\psi]$ in Eq. (20) in the form

$$\begin{aligned} J[\psi] &= J_0 + \sum_{\mathbf{m}} J_{\mathbf{m}} \exp(i\mathbf{m}\xi) = J_0 - \frac{2e^2 N^3 V a^3}{\Omega_{\parallel}^2 \pi^4 \alpha^6} \sum_{\mathbf{m}} |\psi_{\mathbf{m}/4}|^4 \exp(i\mathbf{m}\xi) \\ &\times \iiint \exp -\frac{1}{2\alpha^2}\left\{\frac{\mathbf{m}^2}{4} + \mathbf{K}_1^2 + \mathbf{K}_2^2 + |\mathbf{K}_2 + \mathbf{K}_0|^2 + |\mathbf{K}_1 - \mathbf{K}_0|^2\right\}\left\{\left(\pi_{1\varkappa}^{(1)^2} - \pi_{2\varkappa}^{(1)^2}\right)\right. \\ &\times \frac{\mathbf{K}_0^2 - \mathbf{m}^2/4}{(\mathbf{K}_0^2 + \mathbf{m}^2/4)^2 - (\mathbf{K}_0\mathbf{m})^2} + 2\sum_{q} \frac{\psi_{\mathbf{q}-\mathbf{m}/4}}{\psi_{\mathbf{m}/4}}\left[(\pi_{1\varkappa}^{(1)} + \pi_{2\varkappa}^{(1)})^2 \frac{[\mathbf{q} - (\mathbf{m}/2) - \mathbf{K}_0][(\mathbf{m}/2) - \mathbf{K}_0]}{[\mathbf{q} - (\mathbf{m}/2) - \mathbf{K}_0]^2 [(\mathbf{m}/2) - \mathbf{K}_0]^2}\right. \\ &\left.\left. + (\pi_{1\varkappa}^{(1)} - \pi_{2\varkappa}^{(1)})^2 \frac{[\mathbf{q} - (\mathbf{m}/2) + \mathbf{K}_0][(\mathbf{m}/2) + \mathbf{K}_0]}{[\mathbf{q} - (\mathbf{m}/2) + \mathbf{K}_0]^2 [(\mathbf{m}/2) + \mathbf{K}_0]^2}\right]\right\} d\mathbf{K}_1\, d\mathbf{K}_2\, d\mathbf{K}_0; \quad \Omega_{\parallel}^2 = \frac{\mu a^3}{e^2}\omega^2. \end{aligned} \tag{23}$$

The integration over dK_1 and dK_2, as well as that over the angles of the vector K_0 is now performed directly. The terms with $\pi_{1\varkappa}^{(1)^2} + \pi_{2\varkappa}^{(1)^2}$ in the sum over $\mathbf{q}$ may be joined by pairs and the integration over K_0 can be taken over all space. The integral over $|\mathbf{K}_0|$ in the principal term and in the next largest ones with $\mathbf{q} = \mathbf{m}$ has been calculated by Simpson's method. Finally, in the terms with $\mathbf{q} \neq \mathbf{m}$ the quantity K_0 is neglected compared with $\mathbf{m}/2$ and $\mathbf{q} - \mathbf{m}/2$, as a result of which the results obtained by calculation are somewhat too large for these terms.

The magnitudes of α, a, $\pi_{1\varkappa}^{(1)}$, $\pi_{2\varkappa}^{(1)}$, and $\Omega_{\|}^2$ are taken from previous works[2,16,17]. The results of the calculation are shown in Table 1. As can be seen by comparison of the last three columns, the convergence of the series in q, q'is found to be quite slow, so that the results are quite rough. This is related to the rapid oscillation of the Na and K atomic functions near zero, and the insufficiently rapid decrease of the $\psi_{\mathbf{K}}$. At the same time the number of terms increases rapidly as $\mathbf{q} \neq 0$ and $\mathbf{q}' \neq 0$.

TABLE I

Crystal	$\alpha \cdot 10^{-8}$	$a \cdot 10^{8}$	$\Omega_{\|}^2$	$J'_{\mathbf{m}} \cdot 10^4$,eV $\mathbf{p}'' = 0$, $\mathbf{m}$	$J''_{\mathbf{m}} \cdot 10^4$,eV $\mathbf{q} = \mathbf{m}$	$J'''_{\mathbf{m}} \cdot 10^4$,eV $\mathbf{q} \neq \mathbf{m}$	$J_{\mathbf{m}} \cdot 10^4$, eV Total
NaCl	0.359	2.82	5.320	—132.0	23.4	45.9	—62.7
KCl	0.233	2.14	6.487	— 1.086	—0.370	0.444	— 1.012
KBr	0.205	3.30	6.335	— 0.5108	—0.0859	0.2102	— 0.3865
KJ	0.196	3.53	6.186	— 0.7876	—0.0529	0.4139	— 0.4266

TABLE II.

Crystal	$\pi_{1\varkappa}^{(1)}$	$\pi_{2\varkappa}^{(1)}$	$J'_{\mathbf{m}} \cdot 10^4$, eV $\mathbf{p}'' = 0$, $\mathbf{m}$	$J''_{\mathbf{m}} \cdot 10^4$, eV $\mathbf{q} = \mathbf{m}$	$J'''_{\mathbf{m}} \cdot 10^4$, eV $\mathbf{q} \neq \mathbf{m}$	$J_{\mathbf{m}} \cdot 10^4$, eV Total
NaCl	0.592	—0.124	—185.7	—13.3	39.7	—159.3
KCl	0.420	0.092	— 0.9612	— 0.3782	0.0676	— 1.272
KBr	0.628	—0.161	— 0.5741	— 0.1618	0.0468	— 0.6891
KJ	0.732	—0.305	— 1.186	— 0.395	0.152	— 1.429

For a more reliable calculation of $J_{\mathbf{m}}$, we calculated it according to Eq. (23) with the aid of smoother cation functions, as proposed by Slater[22], namely $\psi_a(r) \sim r^n e^{-\alpha_n r}$, where $n = 2$ and 2.7, $a_n = 0.733/a_B$ and $0.55/a_B$ for Na and K, respectively. (For convenience, the number 2.7 was rounded out to 3.) Then

$$\text{Na:}\quad \psi_{\mathbf{K}} = \sqrt{\frac{8\pi\alpha}{5}}\,\frac{16\,\alpha^4 a_b^6}{V}\,\frac{\alpha^2 a_b^2 - K^2 a_b^2}{[\alpha^2 a_b^2 + K^2 a_b^2]^4}\,;$$

$$\text{K:}\quad \psi_{\mathbf{K}} = \sqrt{\frac{4\pi\alpha}{35}}\,\frac{16\alpha^4 a_b^6}{V}\,\frac{5a_b^4\alpha^4 - 10\,\alpha^2 K^2 a_b^4 + K^4 a_b^4}{[\alpha^2 a_b^2 + K^2 a_b^2]^5}\,. \tag{24}$$

The calculation was performed using the same Eq. (23), except with different values of $\psi_{\mathbf{m}/4}$ and $\psi_{\mathbf{q}-\mathbf{m}/4}$.

As can be seen from the result shown in Table 2, the correction terms here decrease somewhat more rapidly and therefore the value obtained for $J_{\mathbf{m}}$ is more reliable.

For KCl, KBr, and KI crystals, in which the polaron radius is relatively large, the Fourier coefficients $J_{\mathbf{m}}$ are small compared with the kinetic energy $\hbar^2 K^2/2M$ of the "free" polaron, and the solution of Eq. (2) may be obtained with the approximation of almost free electrons. Then the forbidden band width is $2|J_{\mathbf{m}}|$, which is much less than both the minimum and maximum widths of the first allowed band, namely $3\hbar^2\pi^2/2Ma^2$ and $5\pi^2\hbar^2/2Ma^2$. Therefore the first allowed band should overlap the second. All higher bands overlap even more. One may thus conclude that for polarons whose quantum state radius $1/\alpha \geq 1.5a$, the band structure of the energy spectrum is of no significance. The spectrum consists of close-lying and overlapping allowed bands with narrow (10^{-3} ev) gaps. On the average the energy is described approximately by Eq. (1).

In the NaCl crystal $1/\alpha \approx a$, and the oscillations of $J(\xi)$ are comparable with the mean kinetic energy. The approximation of "almost free electrons" is not applicable to a solution of Eq. (2). One may expect measurable energy gaps between the lowest allowed bands. The energy gaps are even wider for small-radius polarons (LiF, BaO crystals, etc.). For them, however, as for NaCl, the present calculation gives results which are too approximate, since the EMM is not a sufficiently good zeroth approximation. Here the question of the energy spectrum structure goes over into the problem of constructing a small-radius polaron theory.

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186