THEORY OF POLARONS IN MANY-VALLEY CRYSTALS

I. WEAK INTERACTION BETWEEN ELECTRON AND LATTICE POLARIZATION FIELD

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The theory of polarons is discussed for the case of many-valley cubic crystals. The case of weak coupling between electron and polarization vibrations of the crystal lattice and the case of a large-radius polaron are considered. The energy of the polaron state and the polaron's anisotropic effective mass are calculated. The anisotropy of the latter decreases with increase of the coupling constant. The contribution of virtual inter-valley and interband transitions to the polaron effect is estimated. In the case of a large-radius polaron, this contribution turns out to be small and is neglected.

By weak interaction is to be understood the case when the electron-phonon coupling is small and can be considered in theory as a small perturbation. Historically the strong-coupling theory of polarons was developed first.[1-8] Then the case of weak coupling was considered.[9-15] Mathematically the most difficult case is that of intermediate coupling for which, so far, there are no systematic approximation methods. For this case there have been a number of attempts to calculate the ground state energy of a conduction electron in an inertially polarizable medium by using direct variational methods. In this connection, certain approximations (see, for example,[11,12]) go over into the well-known, correct results in the limiting case of weak coupling whereas in the case of strong-coupling they are very far from the correct results. These approximations are applicable only for sufficiently weak coupling.

Other approximations[16-20] lead to the correct results both for the case of weak coupling and for the strong-coupling case. Therefore, one cannot exclude the possibility that among these approximations there may be one which yields a good interpolation even for the case of intermediate coupling. As usual, in using a direct variational method to calculate the energy one must prefer that approximation which yields the lowest value for the ground-state energy. In the intermediate-coupling regime (for $\alpha \sim 5$) this approximation is the one considered in[18]. For calculation of the polaron mobility, the most successful approximation turns out to be the one mentioned in[17,21,22].

In the articles mentioned above, it was assumed that the conduction-electron equal-energy surfaces in k-space are spheres, and the electron effective mass is isotropic. However, study of semiconductors in recent years has shown that even in the case of cubic crystals the conduction band often has a many-valley structure, and in each valley the electron effective mass is anisotropic. Therefore, a generalization of polaron theory to the case of many-valley cubic crystals is of interest.

In this article we consider the simpler case of weak coupling,[1)] and in a subsequent article we shall consider the strong-coupling and intermediate-coupling cases. The effective-mass approximation for the electron will not be used at the beginning of this work, which enables us to estimate the role of inter-valley and interband electron transitions. Calculation of intra-valley transitions will be carried out in an effective-mass approximation. The conduction electron—the "spare" electron—will be treated in the one-electron approximation of band theory.

The energy operator of the system has the form

$$H = H_0(\mathbf{r}) + \hbar\omega \sum_{\varkappa} a_{\varkappa}^{+} a_{\varkappa} + \sum_{\varkappa} (V_{\varkappa} a_{\varkappa} e^{i\varkappa\mathbf{r}} + V_{\varkappa}^{*} a_{\varkappa}^{+} e^{-i\varkappa\mathbf{r}}), \quad (1)$$

where $H_0(\mathbf{r})$ is the energy operator for an electron in a periodic field (with the nuclei fixed at the lattice sites), the second term in (1) represents the energy operator for longitudinal, optical phonons in an ionic crystal, ω denotes the phonon frequency (we neglect dispersion of their frequencies), κ denotes the phonon wave vector, a_{κ}^{+} and a_{κ} are boson creation and annihilation operators for the phonons. The third term in (1) represents the electron-phonon interaction operator, the V_{κ} are the coefficients of the electron-phonon coupling. In the continuum theory of polarons

$$V_{\varkappa} = \frac{e}{|\varkappa|} \sqrt{\frac{2\pi\hbar\omega}{v}\left(\frac{1}{n^2} - \frac{1}{\varepsilon}\right)}, \quad (2)$$

where e is the electron's charge, ϵ is the dielectric constant, n is the index of refraction of light, v is the elementary volume over which periodic boundary conditions are applied.

The third term in (1) is regarded as a small perturbation. In the zero-order approximation, the energy and the states of the system have the following form:

$$E_{m\mathbf{K}\ldots n_{\varkappa}\ldots} = E_m(\mathbf{K}) + \hbar\omega \sum_{\varkappa} n_{\varkappa},$$

$$\psi_{m\mathbf{K}}\Phi_{\ldots n_{\varkappa}\ldots} \equiv |\, m\mathbf{K} \ldots n_{\varkappa} \ldots\rangle, \quad \psi_{m\mathbf{K}}(\mathbf{r}) = \frac{1}{\sqrt{v}} U_{m\mathbf{K}}(\mathbf{r})\, e^{i\mathbf{K}\mathbf{r}}. \quad (3)$$

[1)] In this article the continuum theory of polarons possessing a sufficiently large radius in comparison with the lattice constant is considered.

Here $\psi_{\mathbf{mK}}$ denotes the Bloch wave function of a band electron, m is the band index, K is the quasimomentum of the electron, $E_m(\mathbf{K})$ is its energy, $\Phi \ldots n_{\mathbf{\kappa}} \ldots$ is the wave function of the longitudinal, optical, lattice vibrations, the $n_{\mathbf{\kappa}}$ are the oscillator quantum numbers.

Let $T_{\mathbf{n}}$ be the translation operator which translates a conduction electron and its polarization potential well in space by an integral lattice vector n. Then

$$T_{\mathbf{n}} f(\mathbf{r}, \ldots, a_{\mathbf{\kappa}}^{+}, \ldots, a_{\mathbf{\kappa}}, \ldots) = f(\mathbf{r}+\mathbf{n}, \ldots, a_{\mathbf{\kappa}}^{+} e^{i\mathbf{\kappa n}}, \ldots, a_{\mathbf{\kappa}} e^{-i\mathbf{\kappa n}}, \ldots). \quad (4)$$

The energy operator (1) is invariant under translations and commutes with $T_{\mathbf{n}}$. Therefore we shall choose the eigenfunctions of (1) so that they are eigenfunctions of $T_{\mathbf{n}}$:

$$T_{\mathbf{n}} \Psi_{\mathbf{k}} = e^{i\mathbf{kn}} \Psi_{\mathbf{k}},$$

where k is the quasimomentum of the system. Only terms with

$$\mathbf{K} + \sum_{\mathbf{\kappa}} \mathbf{\kappa} n_{\mathbf{\kappa}} = \mathbf{k}. \quad (5)$$

enter into the expansion of $\Psi_{\mathbf{k}}$ in terms of $\psi_{\mathbf{mK}} \Phi \ldots n_{\mathbf{\kappa}} \ldots$.

Let us assume that in a perturbed state all $n_{\mathbf{\kappa}} = 0$ (low temperatures). Then, for transitions out of this state only matrix elements of the perturbation of the form

$$\langle m'\mathbf{K} - \mathbf{\kappa} \ldots 1_{\mathbf{\kappa}} \ldots | V | m\mathbf{K} \ldots 0_{\mathbf{\kappa}} \ldots \rangle = V_{\mathbf{\kappa}}^{*} \overline{U^{*}_{m'\mathbf{K}-\mathbf{\kappa}} U_{m\mathbf{K}}},$$
$$V \equiv \sum_{\mathbf{\kappa}} (V_{\mathbf{\kappa}} a_{\mathbf{\kappa}} e^{i\mathbf{\kappa r}} + V_{\mathbf{\kappa}}^{*} a_{\mathbf{\kappa}}^{+} e^{-i\mathbf{\kappa r}}). \quad (6)$$

do not vanish. Here the bar denotes the average value in space.

The first-order correction to the energy of the system is equal to zero. In the second-order approximation, the correction to the energy is given by

$$E^{(2)}_{\mathbf{m}\mathbf{K}\ldots 0_{\mathbf{\kappa}}\ldots} = -\sum_{\mathbf{\kappa} m'} \frac{|V_{\mathbf{\kappa}}|^2 \overline{|U^{*}_{m'\mathbf{K}-\mathbf{\kappa}} U_{m\mathbf{K}}|^2}}{E_{m'}(\mathbf{K}-\mathbf{\kappa}) - E_m(\mathbf{K}) + \hbar\omega}. \quad (7)$$

Let us assume that $E_m(\mathbf{K})$ has several equivalent minima located at the points $\mathbf{K} = \mathbf{K}_{0j}$, where j is an index labelling the valley. Let us assume, furthermore, that the quasimomentum K of the perturbed state is sufficiently close to $\mathbf{K}_{01}$ so that $E_m(\mathbf{K}_{01}) - E_m(\mathbf{K}) + \hbar\omega > 0$. Then for all of the terms in (7), the denominator is positive (generation of phonons is impossible). First we carry out the summation over values of κ corresponding only to intravalley transition, i.e., in the region of small values of $|\kappa|$. In this connection one can approximately set $\overline{U^{*}_{m\mathbf{K}-\mathbf{\kappa}} U_{m\mathbf{K}}} = 1$,

$$E_m(\mathbf{K}-\mathbf{\kappa}) - E_m(\mathbf{K}) = \frac{\hbar^2}{2}\left(\frac{\mathbf{\kappa}_{\perp}^2}{\mu_{\perp}} + \frac{\mathbf{\kappa}_{\parallel}^2}{\mu_{\parallel}}\right) - \hbar^2\left(\frac{\mathbf{q}_{\perp}\mathbf{\kappa}_{\perp}}{\mu_{\perp}} + \frac{\mathbf{q}_{\parallel}\mathbf{\kappa}_{\parallel}}{\mu_{\parallel}}\right),$$
$$\mathbf{q} \equiv \mathbf{K} - \mathbf{K}_{01}. \quad (8)$$

Here it is assumed that for small values of q, the isoenergy surfaces in a valley are ellipsoids of revolution, their axis of revolution being direct along $\mathbf{K}_{01}$; $\kappa_{\parallel}$, $\kappa_{\perp}$ and $q_{\parallel}$, $q_{\perp}$ denote the components of the vectors κ and q along the direction $\mathbf{K}_{01}$ and lying in the plane perpendicular to $\mathbf{K}_{01}$; $\mu_{\parallel}$ and $\mu_{\perp}$ denote the effective masses of a band electron in the corresponding directions. The band subscript m will be omitted whenever the question involves only transitions within the conduction band. Substituting (2) and (8) into (7), changing from a summation to integration over the vallue j = 1, we obtain

$$E^{(2)}_{\mathbf{K}\ldots 0\ldots} = -\frac{e^2}{4\pi^2}\left(\frac{1}{n^2} - \frac{1}{\varepsilon}\right)\int \frac{d^3\mathbf{\kappa}}{\mathbf{\kappa}^2}\left[1 - \frac{\hbar}{\omega}\left(\frac{\mathbf{q}_{\perp}\mathbf{\kappa}_{\perp}}{\mu_{\perp}} + \frac{\mathbf{q}_{\parallel}\mathbf{\kappa}_{\parallel}}{\mu_{\parallel}}\right) + \frac{\hbar}{2\omega}\left(\frac{\mathbf{\kappa}_{\perp}^2}{\mu_{\perp}} + \frac{\mathbf{\kappa}_{\parallel}^2}{\mu_{\parallel}}\right)\right]^{-1}. \quad (9)$$

The region of values $|\kappa| \sim \bar{\kappa}$, where

$$\bar{\kappa} = \left[6\omega/\hbar\left(\frac{2}{\mu_{\perp}} + \frac{1}{\mu_{\parallel}}\right)\right]^{1/2}, \quad (10)$$

gives the basic contribution to this integral. For $\mu_{\perp} = \mu_{\parallel}$ and equal to the free-electron mass and $\omega = 10^{13}$ sec^{-1}, one obtains $\kappa \sim 4 \times 10^6$ cm^{-1} which is much smaller than the reciprocal lattice constant. This justifies approximation (8) and allows us in (9) to extend the integration with respect to $|\kappa|$ to ∞. As a result of integration and quadratic expansion of the energy in powers of q one obtains

$$E_{\mathbf{K}\ldots 0\ldots} = E(\mathbf{K}) + E^{(2)}_{\mathbf{K}\ldots 0\ldots} + \ldots = E(\mathbf{K}_{01}) - \alpha\hbar\omega\varphi_0\left(\frac{\mu_{\parallel}}{\mu_{\perp}}\right) + \frac{\hbar^2}{2}\left(\frac{\mathbf{q}_{\perp}^2}{M_{\perp}} + \frac{\mathbf{q}_{\parallel}^2}{M_{\parallel}}\right) + \ldots, \quad (11)$$

where

$$\alpha = \frac{e^2}{\hbar}\sqrt{\frac{\mu_{\perp}}{2\hbar\omega}}\left(\frac{1}{n^2} - \frac{1}{\varepsilon}\right), \quad \frac{1}{M_{\perp}} = \frac{1}{\mu_{\perp}}\left[1 - \frac{\alpha}{6}\varphi_{\perp}\left(\frac{\mu_{\parallel}}{\mu_{\perp}}\right) + \ldots\right],$$
$$\frac{1}{M_{\parallel}} = \frac{1}{\mu_{\parallel}}\left[1 - \frac{\alpha}{6}\varphi_{\parallel}\left(\frac{\mu_{\parallel}}{\mu_{\perp}}\right) + \ldots\right]; \quad (12)$$

$$\varphi_0(x) = \frac{1}{2}\sqrt{\frac{x}{1-x}}\ln\frac{1+\sqrt{1-x}}{1-\sqrt{1-x}} = \sqrt{\frac{x}{x-1}}\operatorname{arctg}\sqrt{x-1}, \quad (13)$$

$$\varphi_{\perp}(x) = \frac{3}{2}\frac{x^{3/2}}{(1-x)^{3/2}}\left[\frac{\sqrt{1-x}}{x} - \frac{1}{2}\ln\frac{1+\sqrt{1-x}}{1-\sqrt{1-x}}\right] =$$
$$= \frac{3}{2}\frac{x^{3/2}}{(x-1)^{3/2}}\left[\operatorname{arctg}\sqrt{x-1} - \frac{\sqrt{x-1}}{x}\right], \quad (14)$$

$$\varphi_{\parallel}(x) = \frac{3\sqrt{x}}{(1-x)^{3/2}}\left[\frac{1}{2}\ln\frac{1+\sqrt{1-x}}{1-\sqrt{1-x}} - \sqrt{1-x}\right] =$$
$$= \frac{3\sqrt{x}}{(x-1)^{3/2}}[\sqrt{x-1} - \operatorname{arctg}\sqrt{x-1}]. \quad (15)$$

Now in the sum (7) let us consider the terms corresponding to inter-valley transitions from valley 1 to valley 2. As a consequence of the equivalence of these valleys, to each point $\mathbf{K}' = \mathbf{K} - \mathbf{\kappa}'$ of the first valley one can associate that point $\mathbf{K}'' = \mathbf{K} - \mathbf{\kappa}''$ at which the energy of a band electron has the same value: $E(\mathbf{K} - \mathbf{\kappa}'') = E(\mathbf{K} - \mathbf{\kappa}')$. Thus, to each term of the intravalley sum considered above with index κ', there is associated a term of the inter-valley sum κ'', having the same denominator. The numerators of these terms differ substantially since $|\kappa'|$ in the present region is of the order of (10), that is, much smaller than the reciprocal lattice constant, but $|\kappa''|$ is of the order of the reciprocal lattice constant.

Therefore

$$\overline{|U^{*}_{\mathbf{K}-\mathbf{\kappa}''} U_{\mathbf{K}}|} < \overline{|U^{*}_{\mathbf{K}-\mathbf{\kappa}'} U_{\mathbf{K}}|} \approx 1, \quad |V_{\mathbf{\kappa}''}|^2/|V_{\mathbf{\kappa}'}|^2 = \mathbf{\kappa}'^2/\mathbf{\kappa}''^2 \sim \mathbf{\kappa}'^2 a^2 \ll 1, \quad (16)$$

where a is the lattice constant.

From here it follows that a term of the inter-valley sum is much smaller than the corresponding term of the intravalley sum, barring the region of large values

$x=\mu_\parallel/\mu_\perp$	$\varphi_0(x)$	$\varphi_\perp(x)$	$\varphi_\parallel(x)$	$x=\mu_\parallel/\mu_\perp$	$\varphi_0(x)$	$\varphi_\perp(x)$	$\varphi_\parallel(x)$
10	1.3166	1.6672	0.6152	1,2	1.0299	1.0531	0.9832
9	1.3056	1.6406	0.6354	1,0	1.0000	1.0000	1.0000
8	1.2930	1.6105	0.6580	0,9	0.9824	0.9684	1.0098
7	1.2779	1.5749	0.6839	0,8	0.9626	0.9326	1.0227
6	1.2600	1.5331	0.7137	0,7	0.9396	0.8945	1.0300
5	1.2378	1.4823	0.7487	0,6	0.9132	0.8500	1.0397
4.5	1.2245	1.4524	0.7687	0,5	0.8813	0.7994	1.0451
4.0	1.2087	1.4175	0.7913	0,4	0.8419	0.7392	1.0474
3.5	1.1913	1.3792	0.8155	0,3	0.7922	0.6644	1.0477
3.0	1.1700	1.3335	0.8431	0,2	0.7229	0.5678	1.0304
2.5	1.1439	1.2787	0.8744	1/6	0.6907	0.5277	1.0167
2.0	1.1110	1.2112	0.9096	1/7	0.6647	0.4956	1.0037
1.8	1.0940	1.1768	0.9285	1/8	0.6426	0.4684	0.9910
1.6	1.0762	1.1427	0.9434	1/9	0.6232	0.4457	0.9784
1.4	1.0552	1.1030	0.9599	0,1	0.6045	0.4280	0.9664

of $|\kappa'|$, which does not give an appreciable contribution to the sum (7). Thus, in (7) we neglect the terms corresponding to inter-valley transitions.

In order to estimate the terms in (7) corresponding to interband transitions, to each term $m\kappa$ we associate a term $m'\kappa$ with the same κ but $m' \neq m$. For these terms, the values of $|V_\kappa|^2$ are identical. For large values of $|\kappa|$ on the order of the reciprocal lattice constant, the interband term is of the same order as the intraband term, and one can also neglect it. For small values of $|\kappa|$ on the order of (10), the interband terms $U_{m'\mathbf{K}-\kappa}$ and $U_{m\mathbf{K}}$ are almost orthogonal and

$$\overline{|U^*_{m'\mathbf{K}-\kappa}U_{m\mathbf{K}}|} \ll 1,$$
$$E_{m'}(\mathbf{K}-\varkappa) - E_m(\mathbf{K}) \gg E_m(\mathbf{K}-\varkappa) - E_m(\mathbf{K}) \sim \hbar\omega, \quad m' \neq m. \quad (17)$$

Therefore, the interband term is much smaller than the intraband term, and one can neglect the interband terms in (7).

Thus, under the approximations made above, the energy of the polaron state and the effective masses of the polaron are determined by formulae (11)–(15). The values of the functions φ_0, $\varphi_\perp$, and $\varphi_\parallel$ are given in the table. The minimum of the system's energy (to the approximation considered) remains at the point $\mathbf{k}_{min} = \mathbf{K}_{01}$, independent of the value of α. The polaron-dependent effect changes in the ground state energy and in the effective masses do not depend on $\mathbf{K}_{01}$. As a result of the polaron effect the effective masses $\mu_\perp$ and $\mu_\parallel$ of a band electron obtain positive corrections, where the smaller of the masses receives the larger correction. As a consequence, the difference between the effective masses decreases with increasing strength of the electron-phonon coupling constant α. Correct to terms of first order in α

$$\frac{M_\parallel}{M_\perp} = \frac{\mu_\parallel}{\mu_\perp}\left\{1 + \frac{\alpha}{6}\left[\varphi_\parallel\left(\frac{\mu_\parallel}{\mu_\perp}\right) - \varphi_\perp\left(\frac{\mu_\parallel}{\mu_\perp}\right)\right] + \ldots\right\}. \quad (18)$$

This formula together with the Table shows that the anisotropy of the polaron effective masses decrease with increase of α.

In a subsequent article devoted to the strong-coupling and intermediate-coupling cases, the following questions will be clarified in a more general model and with inter-valley transitions taken into consideration: Whether the ratio $M_\parallel/M_\perp$ tends to unity with increasing values of α, whether $\mathbf{k}_{min}$ tends to zero, or whether these quantities tend to other limits.

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219