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Electronic Polarons in Alkali Halides[*]

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The effect of electronic polarization on an electron in the s-like conduction band, described by the tight-binding approximation, is studied using both the Green's function and perturbation methods. A criterion for the validity of the second-order perturbation method is derived. It turns out that the second-order perturbation method is valid even for large values of the coupling constant due to the exciton energy being considerably larger than the conduction-band width. The behavior of the polaron band and effective mass is examined as a function of the coupling constant, of the parameter λ, which represents the extent of localization of the atomic orbital, and of the exciton energy. For a given crystal, polarization effects are found to increase as the wave vector $\vec{k}$ increases. The present results are compared with previous results which apply only near $\vec{k}=0$, and with the results obtained by classical theory.

I. INTRODUCTION

In analogy with the lattice polaron,[1] Toyozawa[2] introduced the concept of the electronic polaron – an extra electron dressed with virtual excitons. The dimensionless coupling constant α characterizing the strength of interaction between the extra electron and virtual excitons was found for the alkali halides to be less than 1. Thus, according to the usual criterion for these crystals, the electronic polaron problem lies in the region of weak-coupling theory. Toyozawa has used his idea of the electronic polaron and the intermediate coupling method to study the effect of electronic polarization on the state of a low-momentum conduction electron in the effective-mass approximation. The purpose of this work is to study the effect of the electronic polarization on the state of a conduction electron of arbitrary momentum, i.e., on the whole conduction band, for both CsCl-type and NaCl-type crystals. This study is carried out by using the basic concept of Toyozawa's electronic polaron within the framework of the tight-binding approximation. We are particularly interested in (a) the shape and position of the polaron band as a function of the electronic wave vector $\vec{k}$, the exciton energy ϵ, and the parameter λ' in the atomic orbital [to be defined in Eq. (15)] and (b) the effective mass near $k=0$ as a function of ϵ and λ'.

In Sec. II A, we use the Green's-function approach based on approaches developed in Refs. 3 and 4 for the lattice polaron problem, to obtain the polaron band $E_p(\vec{k})$ for arbitrary $\vec{k}$. Ordinary perturbation theory is used in Sec. II B to obtain $E_p(\vec{k})$ and the effective mass of the electronic polaron. In Sec. III A, we show that second-order perturbation theory is superior to the Green's-function method used in this problem (even for a rather large value of the coupling constant) and derive a criterion for the validity of perturbation theory. Values of the parameters in the theory are estimated in Sec. III B. The general features of the polaron band are discussed in Sec. III C. In this section, we also compare our results with those of Toyozawa,[2] Fowler,[5] and the classical ones of Du Pré *et al.*[6] and of Mott and Littleton.[7] Finally, we discuss the change in the effective mass caused by the electronic polarization as a function of λ', ϵ, and α.

II. FORMALISM AND CALCULATIONS

A. Green's-Function Method

Toyozawa's Hamiltonian[2] for the electronic polaron is of the form

$$H = \left[\frac{p^2}{2m_e} + \sum_{\vec{R}_n} V(\vec{r}-\vec{R}_n)\right] + \epsilon\sum_{\vec{q}} b_{\vec{q}}^{\dagger} b_{\vec{q}} + (-e)\,\phi(r)\,, \tag{1}$$

where $\phi(r)$ is given by

$$\phi(r) = \frac{\epsilon}{e}\left(\frac{4\pi\alpha}{V}\right)^{1/2}\left(\frac{\hbar^2}{2m_b\epsilon}\right)^{1/4}\sum_{\vec{q}}\frac{i}{|\vec{q}\,|} \times \left[b_{\vec{q}}\,e^{i\vec{q}\cdot\vec{r}} - b_{\vec{q}}^{\dagger}\,e^{-i\vec{q}\cdot\vec{r}}\right]\,. \tag{2}$$

The first term in the Hamiltonian describes the extra electron moving under the influence of the periodic potential of the crystal when the ions and the crystal valence electrons are in the ground state. Thus the eigenstates of the first term constitute the conduction band of the crystal in which the electronic and ionic polarizations are not yet taken into account. The second term is the Hamiltonian of the excitons; the energy of each exciton is ϵ irrespective of wave vector $\vec{q}$. The $b_{\vec{q}}^{\dagger}$ and $b_{\vec{q}}$ are, respectively, creation and annihilation operators for excitons of wave vector $\vec{q}$. The last term describes the interaction of the electron at $\vec{r}$ with the excitons; e is the electronic charge, $\hbar$ is Planck's constant divided by 2π, m_b is the effective-band mass of an electron at the bottom of the conduction band when neither the electronic nor the ionic polarization is taken into account, V is the volume of the crystal under consideration, and the dimensionless coupling constant α is defined as

$$\alpha = \frac{1}{2}\left(1 - \frac{1}{\epsilon_\infty}\right)\frac{e^2}{\epsilon}\left(\frac{2m_b\epsilon}{\hbar^2}\right)^{1/2} , \tag{3}$$

where ϵ_∞ is the usual high-frequency dielectric constant.

To reach the Green's-function approach, we shall now use the usual formalism of second quantization and rewrite the Hamiltonian in Eq. (1) in a complete second-quantized form. Adopting the tight-binding approach of Löwdin,[8] we write the crystal orbital of the conduction electron as

$$\psi_{\vec{k}}(r) = G^{-3/2}\sum_{\vec{R}_n} e^{i\vec{k}\cdot\vec{R}_n}\,\Phi(\vec{r}, \vec{R}_n) , \tag{4}$$

where the summation extends over the positive ions only. The $\Phi(\vec{r}, \vec{R}_n)$ are defined in terms of the normalized atomic wave functions $\phi(\vec{r}, \vec{R}_n)$ as follows:

$$\Phi(\vec{r}, \vec{R}_n) = \phi(\vec{r}, \vec{R}_n) - \tfrac{1}{2}\sum_{\vec{R}_m} \phi(\vec{r}, \vec{R}_m)\, S_{nm} , \tag{5}$$

where the S_{nm} have the form

$$S_{nm} = \int \phi(\vec{r}, \vec{R}_n)\phi(\vec{r}, \vec{R}_m)\, d\vec{r} - \delta_{\vec{R}_n\vec{R}_m} . \tag{6}$$

The crystal orbital given by Eq. (4) is exactly orthonormalized (up to and including terms of the first order in the overlap S) in a crystal containing G^3 lattice points. In the case of negligible overlap, $S_{nm} \approx 0$, and Eq. (4) reduces to the usual Bloch sum. In terms of the electron creation and annihilation operators $a^\dagger_{\vec{k}}$ and $a_{\vec{k}}$, respectively, the first term in Eq. (1) can be written as

$$\mathcal{H}_0 = \sum_{\vec{k}} E(\vec{k}) a^\dagger_{\vec{k}} a_{\vec{k}} , \tag{7}$$

where $E(\vec{k})$ is the energy of the electron of wave vector $\vec{k}$ in the tight-binding approximation.[9] In the simple cubic case, which corresponds to the lattice formed by the Cs ions in CsCl, CsBr, and CsI, the $E(\vec{k})$ for the s-like conduction band is given by

$$E(\vec{k}) = -\,|J|\,(\cos k_x a + \cos k_y a + \cos k_z a) , \tag{8}$$

where a is the lattice constant and $|J|$ is an overlap integral, which is estimated from the width of the conduction band (see Sec. III B). We take as our units of energy and length $|J|$ and a, respectively, which implies $\hbar^2/m_b = 1$. In the fcc case, corresponding to crystals with the NaCl structure, the $E(\vec{k})$ for the s-like conduction band is given by

$$E(\vec{k}) = -\,|J'|\,(\cos k_x a \cos k_y a + \cos k_x a \cos k_z a + \cos k_y a \cos k_z a) , \tag{9}$$

where $2a$ is the lattice constant. With units of energy and length of $|J'|$ and a, respectively, we write $\hbar^2/2m_b = 1$.

The last term in Eq. (1) in a complete second-quantized form includes the matrix elements $\langle \psi_{\vec{k}}(r) \,|\, e^{i\vec{q}\cdot\vec{r}} \,|\, \psi_{\vec{k}'}(r)\rangle$ and $\langle \psi_{\vec{k}}(r) \,|\, e^{-i\vec{q}\cdot\vec{r}} \,|\, \psi_{\vec{k}'}(r)\rangle$. The former is of the form

$$\int_G \psi^*_{\vec{k}}(r)\, e^{i\vec{q}\cdot\vec{r}}\, \psi_{\vec{k}'}(r)\, d\vec{r} = G^{-3} \sum_{\vec{R}_m, \vec{R}_l} \exp[i\vec{k}\cdot\vec{R}_l + i(\vec{k}' + \vec{q} - \vec{k})\cdot\vec{R}_m] \times \int \Phi^*(\vec{r}, \vec{R}_l)\, e^{i\vec{q}\cdot\vec{r}}\, \Phi(\vec{r}, 0)\, d\vec{r} , \tag{10}$$

where we have changed the variable of integration. As the Φ's are orthogonal, we expect that the largest contribution occurs when $\vec{R}_l = 0$. Application of Eq. (6) to Eq. (10) yields

$$G^{-3} \sum_{\vec{R}_m} e^{i(\vec{k}' + \vec{q} - \vec{k})\cdot\vec{R}_m}\Big[\int |\phi(\vec{r}, 0)|^2 e^{i\vec{q}\cdot\vec{r}}\, d\vec{r} - \sum_{\vec{R}_m} \int \phi(\vec{r}, \vec{R}_m)\, \phi(\vec{r}, 0)\, e^{i\vec{q}\cdot\vec{r}}\, S_{m0} + \cdots\Big] .$$

The second term is of order $S^2_{\delta 0}$, δ being the nearest-neighbor distance and is neglected. With the aid of the identity

$$\sum_{\vec{R}_m} e^{i(\vec{k}' + \vec{q} - \vec{k})\cdot\vec{R}_m} = G^3 \sum_{\vec{K}_\nu} \delta(\vec{k}' + \vec{q} - \vec{k} - \vec{K}_\nu) ,$$

$\vec{K}_\nu$ being a vector in the reciprocal lattice, we then obtain

$$\langle \psi_{\vec{k}}(r) \,|\, e^{i\vec{q}\cdot\vec{r}} \,|\, \psi_{\vec{k}'}(r)\rangle = \sum_{\vec{K}_\nu} \delta(\vec{k}' + \vec{q} - \vec{k} - \vec{K}_\nu) \int |\phi(\vec{r}, 0)|^2 e^{i\vec{q}\cdot\vec{r}}\, d\vec{r} . \tag{11}$$

Restricting ourselves to the case of $\vec{K}_\nu = 0$ and treating the other matrix element in the same manner, we obtain the interaction term in Eq. (1) in complete second-quantized form as

$$\mathcal{H}_I = \sum_{\vec{k}, \vec{k}'} \langle \psi_{\vec{k}}(r) \,|\, (-e)\,\phi(r) \,|\, \psi_{\vec{k}'}(r)\rangle\, a^\dagger_{\vec{k}+\vec{q}}\, a_{\vec{k}} , \quad = \sum_{\vec{q}, \vec{k}} V_q(0)\, [b^\dagger_{-\vec{q}} - b_{\vec{q}}]\, a^\dagger_{\vec{k}+\vec{q}}\, a_{\vec{k}} , \tag{12}$$

where $V_q(0)$ is given by

$$V_q(0) = \epsilon\left(\frac{4\pi\alpha}{V}\right)^{1/2}\left(\frac{\hbar^2}{2m_b\epsilon}\right)^{1/4}\frac{i}{|\vec{q}\,|} \times \int |\phi(\vec{r}, 0)|^2 e^{i\vec{q}\cdot\vec{r}}\, d\vec{r} . \tag{13}$$

Accordingly, when the electronic part is requantized, the Hamiltonian of the present system is given by

$$\mathcal{H} = \sum_{\vec{k}} E(\vec{k})\, a^\dagger_{\vec{k}} a_{\vec{k}} + \epsilon \sum_{\vec{q}} b^\dagger_{\vec{q}} b_{\vec{q}}$$

$$+\sum_{\vec{q},\vec{k}} V_q(0)\,[b^\dagger_{-\vec{q}}-b_{\vec{q}}]\,a^\dagger_{\vec{k}+\vec{q}}a_{\vec{k}} \ . \qquad (14)$$

Here we note that in the following numerical calculation based on Eq. (14), for simplicity, the atomic orbital $\phi(r)$ in $V_q(0)$ will be approximated by the 1s orbital

$$\phi(r)=(\lambda'^3/\pi)^{1/2}\,e^{-\lambda' r} \ , \qquad (15)$$

determined approximately by the ionization energy of the free alkali atom (see Sec. III B). The 1s orbital determined in this way is approximately 4s-like in character for potassium and 6s-like in Cs.

We now follow the procedure of Pines[3] and Puff and Whitfield[4] to obtain the propagators. Treating the electron exciton interaction as the perturbation, we obtain the following true Green's function:

$$G(\vec{k},\omega)=[\omega-E(\vec{k})-\Sigma(\vec{k},\omega)+i\delta]^{-1} \ . \qquad (16)$$

$G(\vec{k},\omega)$ is the Fourier transform of $G(\vec{k},t)$. As in Ref. 4, we approximate the self-energy Σ by the expression

$$\Sigma(\vec{k},\omega)=\sum_{\vec{q}}\frac{|V_q(0)|^2}{\omega-\epsilon-E(\vec{k}-\vec{q})-\Sigma(\vec{k}-\vec{q},\omega-\epsilon)} \ , \qquad (17)$$

This corresponds to solving the Dyson equation as in Fig. 1. Replacing the summation over $\vec{q}$ by an integration, we obtain an integral equation. This integral equation is too complex to solve exactly. In principle, it can be solved by an iteration process, but this requires a very large amount of computing time even on a high-speed computer.
In calculating $\Sigma^0(\vec{k}-\vec{q},\omega-\epsilon)$ numerically in zeroth order,

$$\Sigma^0(\vec{k}-\vec{q},\omega-\epsilon)=\sum_{\vec{q}'}|V_{q'}(0)|^2/[\omega-2\epsilon-E(\vec{k}-\vec{q}-\vec{q}\,')] \ ,$$

using the E($\vec{k}$) given for the particular set of parameters[10] $\alpha=1$, $\lambda=4$ ($\lambda=\lambda' a$), $x=\epsilon/|J|=12$, we found that Σ^0 is a slowly varying function of $\vec{k}$. Thus, in calculating $\Sigma^1(\vec{k},\omega)$ in first order of our iteration,

$$\Sigma^1(\vec{k},\omega)=\sum_{\vec{q}}\frac{|V_q(0)|^2}{(\omega-\epsilon-E(\vec{k}-\vec{q})-\Sigma^0(\vec{k}-\vec{q},\omega-\epsilon))} \ ,$$

we replaced $\Sigma^0(\vec{k}-\vec{q},\omega-\epsilon)$ by a constant $\bar{\Sigma}(\omega-\epsilon)$, i.e., its average value. This procedure seems reasonable since for the parameters considered $\Sigma^0(\vec{k},\omega)$ and $\Sigma^1(\vec{k},\omega)$ differed by less than 15%. Hence, the main part of $\Sigma(\vec{k},\omega)$ is determined by the value of the zeroth order. Having approximated $\Sigma(\vec{k},\omega)\approx\Sigma^1(\vec{k},\omega)$, we obtain the electronic polaron band

$$z=E_p(\vec{k}) \qquad (18)$$

as a solution of

$$z-E(\vec{k})-\Sigma(\vec{k},z)=0 \ . \qquad (19)$$

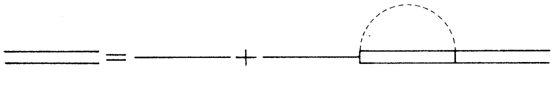

FIG. 1. The Dyson equation is solved approximately as indicated above. Double lines represent true one-electron propagators, and the solid single and broken single lines represent the free-electron and free-exciton propagators, respectively.

B. Perturbation Method

We start with the Hamiltonian given by Eq. (14) and treat the last term of that equation as a small perturbation. So our initial state is one in which no excitons are present, and an electron of wave vector $\vec{k}$ is present. We write this state as

$$|\vec{k},0\rangle=a^\dagger_{\vec{k}}|0\rangle \ , \qquad (20)$$

where $|0\rangle$ is the ground state of the system in which there are no extra electrons and no excitons. Then an intermediate state leading to nonvanishing matrix elements is of the form

$$|\vec{k}',\vec{q}\rangle=a^\dagger_{\vec{k}'}b^\dagger_{\vec{q}}|0\rangle \ , \qquad (21)$$

where $\vec{k}'=\vec{k}-\vec{q}$, so that the intermediate state energy is $E(\vec{k}-\vec{q})+\epsilon$. The second-order perturbation formula leads then immediately to

$$\Delta E^{(2)}(\vec{k})=-\sum_{\vec{q}}\frac{|V_q(0)|^2}{E(\vec{k}-\vec{q})+\epsilon-E(\vec{k})} \ . \qquad (22)$$

We have replaced the summation over $\vec{q}$ by an integration to evaluate $\Delta E^{(2)}(\vec{k})$ on an electronic computer for the directions [100], [110], and [111] in both cubic lattices, using the energy expressions given by Eqs. (8) and (9). In both the simple cubic case and the fcc case, the Brillouin zone was taken as a cube of side $2\pi/a$. Actually, in the fcc case the Brillouin zone is a truncated octahedron of volume $\frac{1}{2}(2\pi/a)^3$. A more reasonable calculation, in which the Brillouin zone was replaced by a sphere of radius π/a, showed that replacing the Brillouin zone by a cube of side $2\pi/a$ caused an overestimate in $\Delta E^{(2)}(\vec{k})$ of order 10%. Qualitatively, no other changes were introduced. The accuracy of the numerical calculations was estimated to be ~10%.

The fourth-order energy has been calculated (the odd orders vanish) to be

$$\Delta E^{(4)}(\vec{k}) = \sum_{\vec{q},\vec{q}'} \frac{|V_{q'}(0)|^2 |V_q(0)|^2}{(E(\vec{k}) - E(\vec{k}-\vec{q}) - \epsilon)^2 (E(\vec{k}) - E(\vec{k}-\vec{q}-\vec{q}\,') - 2\epsilon)}$$
$$+ \sum_{\vec{q},\vec{q}'} \frac{|V_{q'}(0)|^2 |V_q(0)|^2}{(E(\vec{k}) - E(\vec{k}-\vec{q}\,') - \epsilon)(E(\vec{k}) - E(\vec{k}-\vec{q}-\vec{q}\,') - 2\epsilon)(E(\vec{k}) - E(\vec{k}-\vec{q}) - \epsilon)}$$
$$- \left(\sum_{\vec{q}'} \frac{|V_{q'}(0)|^2}{(E(\vec{k}) - E(\vec{k}-\vec{q}\,') - \epsilon)^2} \right) \left(\sum_{\vec{q}} \frac{|V_q(0)|^2}{E(\vec{k}) - E(\vec{k}-\vec{q}) - \epsilon} \right) . \tag{23}$$

The fourth-order energy is evaluated at $k = 0$ partially analytically and partially numerically for the particular set of parameters $\alpha = 2$, $\lambda = 4$, and $x = \epsilon / |J| = 12$ by using the effective-mass approximation and the approximation of replacing $|q_{\max}|$ by ∞. In this way, we find that $\Delta E^{(4)}(0) = 0.005$ and $\Delta E^{(2)}(0) = 9.4$. This means that the contribution from the fourth order is negligible. We note that the fourth-order term is identically zero when the bandwidth is much less than ϵ. This corresponds to the physical case as the bandwidth of the s-like conduction band is considerably less than the exciton energy.

The values of $E_p(\vec{k})$ versus $\vec{k}$, based on the second-order perturbation result, are shown in Figs. 2 and 3.

Expanding the second-order energy shift about $k = 0$ in terms of a power series in k, we obtain

$$m_p / m_b = (1 - \chi)^{-1} , \tag{24}$$

which shows the change in effective mass caused by the electronic polarization. m_p is known as the mass of the electronic polaron. The χ in its simplest form in normalized units is

$$\chi = \alpha x^2 \left(\frac{1}{2x} \right)^{1/2} \frac{(4\lambda^2)^2}{2\pi^2} \int_{-\pi}^{\pi} \iint \frac{d\vec{q}}{q^2 (4\lambda^2 + q^2)^4 (x + 3 + E(\vec{q}))^2} \left[\frac{2 \sin^2 q_x}{x + 3 + E(\vec{q})} - \cos q_x + 1 \right] \tag{25}$$

for the simple cubic case and

$$\chi = \alpha x^2 \left(\frac{1}{x} \right)^{1/2} \frac{(4\lambda^2)^4}{2\pi^2} \int_{r=0}^{\pi} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} \frac{d\vec{q}}{q^2 (4\lambda^2 + q^2)^4 (x + 3 + E(\vec{q}))^2} \left[\frac{2 \sin^2 q_x (\cos^2 q_y + \cos q_y \cos q_z)}{E(\vec{q}) + x + 3} - \cos q_x \cos q_y + 1 \right] \tag{26}$$

for the fcc case.

III. DISCUSSION AND CONCLUSION

A. Comparison of Green's-Function and Perturbation Methods

We compare the relative merits of the Green's-function and perturbation methods. As shown in Fig. 2, the $E_p(\vec{k})$ predicted from the Green's-function method is higher than that predicted from the second-order perturbation method for the same set of parameters. As the energy shift corresponds to the self-energy of the electron, the self-energy obtained from perturbation theory is thus larger. Then taking this fact as a variational criterion, we conclude that the second-order perturbation theory gives a better result than this Green's-function approach. A similar result has been found by Puff and Whitfield[4] in the case of the lattice polaron. It is not surprising that the Green's-function method yields a higher energy than the second-order perturbation method. The reason is the following. In the Green's-function method only a particular class of diagrams is summed. In contrast, in the above perturbation method more terms are taken into account [for example, in Eq. (23) only the first term is included in the Green's-function method]. However, the three terms in the fourth order nearly cancel each other [see the discussion following Eq. (23)], even though each term itself is not negligible. Thus in this Green's-function approach we are not summing over all the physically important diagrams and we conclude that for the present problem the second-

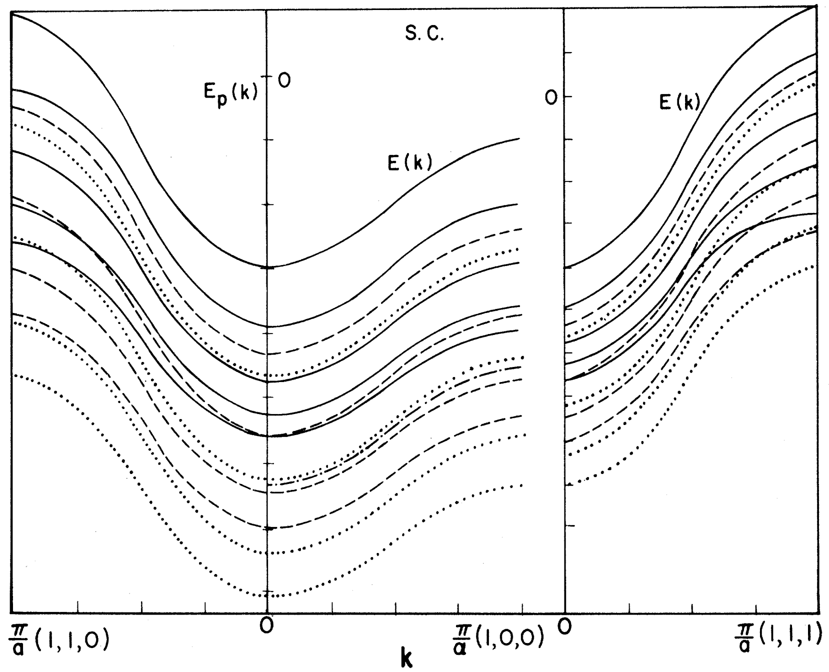

FIG. 2. The polaron band $E_p(\vec{k})$ is plotted in units of $|J|$ for $\alpha=1$ in the simple-cubic case. The top line $E(\vec{k})$ refers to the unperturbed band. Sets of solid lines refer to values of $x=6$, broken lines to values of $x=12$, and dotted lines to values of $x=18$. The four lines in each set correspond from the top one down to values of $\lambda=1$, $\lambda=2$, $\lambda=3$, $\lambda=4$, respectively (see also Ref. 10). The dotted-dashed line in the [1 0 0] direction corresponds to the Green's-function result for $\alpha=1$, $x=12$, $\lambda=4$.

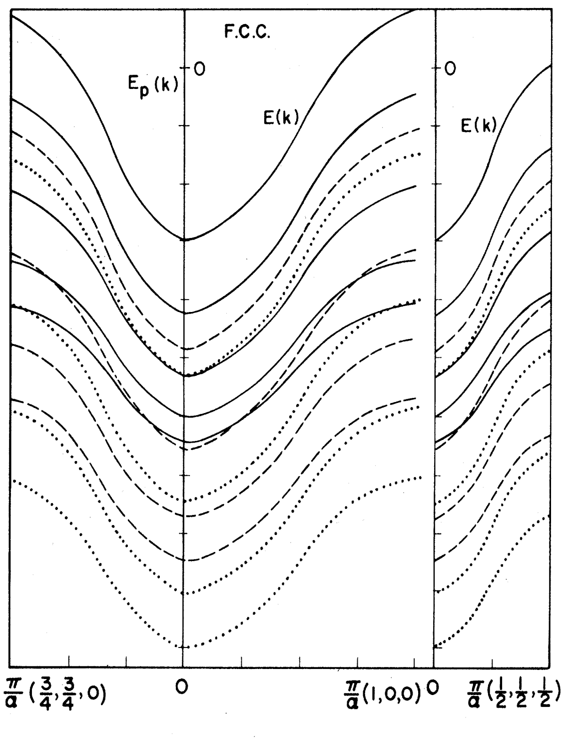

FIG. 3. The polaron band $E_p(\vec{k})$ is plotted in units of $|J|$ for $\alpha=1$ in the fcc case. The top line $E(\vec{k})$ refers to the unperturbed band. Sets of solid lines refer to values of $x=6$, broken lines to values of $x=12$, and dotted lines to values of $x=18$. The four lines in each set correspond from the top one down to values of $\lambda=1$, $\lambda=2$, $\lambda=3$, $\lambda=4$, respectively (see also Ref. 10).

order perturbation result is more reasonable. This conclusion is supported by the following discussion. In the theory of nuclear forces, the Hamiltonian for the interaction of a nucleon with neutral mesons has the same form as our Hamiltonian. Wentzel[11] has shown that in the case of no recoil, the second-order perturbation result obtained from such a Hamiltonian is exact. No recoil effect corresponds in the present problem to the physical fact that the conduction-band width is considerably less than the exciton energy.

We now discuss the regions of α in which the application of second-order perturbation theory to the electronic polaron problem is valid. There are several criteria we could use. We start with the usual criterion based on the second-order shift. Using the effective-mass approximation, the replacement of $|q_{\max}|$ by ∞, and

$$V_q(0)=\epsilon\left(\frac{4\pi\alpha}{V}\right)^{1/2}\left(\frac{\hbar^2}{2m_b\epsilon}\right)^{1/4}\frac{i}{|\vec{q}|}$$

[derived from Eq. (13) by neglecting the atomic nature of the electronic function], we obtain from Eq. (22) the energy shift at the bottom of the conduction band to be $\alpha\epsilon$. The result is in agreement with that predicted from Toyozawa's theory. For this energy shift the number of virtual excitons around the extra electron is $\langle N\rangle=\frac{1}{2}\alpha$. The unperturbed state of the electron without polarization is E_0, which is of the order of the exciton energy ϵ. Therefore, the energy of the perturbed state of the system is $E_0-\alpha\epsilon+\frac{1}{2}\alpha\epsilon$. For the perturbation to be small we require $E_0\gg|-\frac{1}{2}\alpha\epsilon|$ or $\alpha\ll 2$. This is a rather stringent condition on α compared with one obtained next, from another point of view. By use of the effective-mass approximation [i. e., $E(q)\propto q^2$],

$$V_q(0)=\epsilon\left(\frac{4\pi\alpha}{V}\right)^{1/2}\left(\frac{\hbar^2}{2m_b\epsilon}\right)^{1/4}\frac{i}{|\vec{q}\,|},$$

and $|q_{\max}|=\pi$, we obtain, from the power series in terms of q^2/x for the fourth-order term given by Eq. (23), $\Delta E^{(4)}(0)\simeq\alpha^2/x^2$. In applying perturbation theory, we require $\Delta E^{(4)}(0)$ to be much less than the second-order energy $\Delta E^{(2)}(0)$. In the same approximation $\Delta E^{(2)}(0)$ is found to be $\alpha x(2/\pi)\times\tan^{-1}(\pi/\sqrt{2}x)$. As x is large (see Sec. III B) we can set $\alpha x(2/\pi)\tan^{-1}(\pi/\sqrt{2}x)\simeq\alpha x^{1/2}$. Thus we get the criterion $\alpha^2/x^2\ll\alpha x^{1/2}$ or $\alpha\ll x^{5/2}$. This criterion can be written in another form. The classical electron self-energy is of order $[e^2/2(0.6a)]\times(1-1/\epsilon_\infty)$.[12] Denoting this self-energy divided by $|J|$ by P – the normalized electron self-energy – and writing

$$\alpha=\frac{1}{2}\left(1-\frac{1}{\epsilon_\infty}\right)\frac{e^2}{a}\,\frac{2}{|J|\sqrt{x}}$$

[from Eq. (3) upon noting $m_b=\hbar/|J|a^2$], we obtain $\alpha\simeq P/\sqrt{x}$. Thus in terms of P the criterion $\alpha\ll x^{5/2}$ can be reduced to $P\ll x^3$. This criterion implies that when the normalized electron self-energy is much less than the cube of the normalized exciton energy, the perturbation method is always valid. In other words, perturbation theory is valid in the electronic polaron problem even for insulators with large values of α. Of course, this is not the case in the lattice polaron problem. The discrepancy is due to the fact that the exciton energies are considerably larger than typical phonon energies (exciton energy ~ 7 eV, phonon energy ~0.03 eV, typically).

B. Estimate of Realistic Values of α, λ, $|J|$

α is defined in Eq. (3). All quantities contained in that equation are well known except m_b. In the present calculation the value for m_b is obtained from those given in Refs. 13, 14, and 16. For these values and the consequent values of α see Table I.

The nondimensional λ we use in our calculations is defined as $\lambda=\lambda' a$, where a is defined in Sec. II A. The λ' is determined by setting the observed ionization energy of the alkali metals of interest equal to $e^2/2\langle r\rangle=\frac{1}{2}e^2\lambda'$, which is the ionization energy for a hydrogenlike 1s orbital. The values of λ determined are summarized in Table II. These values are about half of λ in the real hydrogenic 1s function. Thus the determined 1s orbital is much more diffuse than the real hydrogenic 1s function and is likely to be the orbital of the valence electron in character.

TABLE I. Values of the calculated coupling constant, the exciton energy ϵ in eV (corresponding to the experimental values of the lowest exciton peak given in Ref. 15), the optical dielectric constant ϵ_∞ (Ref. 12) and m_b/m_e. The value of m_b/m_e is taken (a) for KCl and KBr from the cyclotron resonance data of Hodby (Ref. 13), (b) for KI from Hodby *et al.* (Ref. 13), and (c) for CsI from the theoretical value of Onodera (Ref. 16).

	KCl	KBr	KI	CsI
ϵ	7.76	6.77	5.80	5.76
ϵ_∞	2.13	2.33	2.69	3.03
m_b/m_e	0.48	0.39	~0.398	0.42
α	0.48	0.49	0.61	0.66

The value of $|J|$ may be determined from the s-like conduction-band width in a particular direction. Philips[18] has attempted to use the ultraviolet absorption spectra of alkali halides to deduce the band structure. The s-like bandwidths in [100] direction for KCl, KBr, and KI were found to be 3.3, 2.6, and 2.0 eV, respectively. From this we obtain $|J|$ equal to 0.83 eV for KCl, 0.65 eV for KBr, and 0.5 eV for KI. The normalized exciton energies denoted by $x=\epsilon/|J|$ are summarized in Table III. More reliable band calculations performed on KCl,[19] KI,[20] and CsI[21] have shown that a single parameter $|J|$ does not suffice to describe the band structure, so that the tight-binding approximation may not be too reliable in the case of the alkali halides. We thus expect our results to be semiquantitative, i.e., the present calculation is an order-of-magnitude calculation. This, however, does not affect the conclusions drawn or the qualitative features of the polaron band.

C. Features of $E_p(\vec{k},\alpha,\lambda,x)$

We have plotted $E_p(\vec{k},\lambda,x)$ [obtained from Eqs. (8), (9), (13), (15), and (22)] versus $\vec{k}$ in Fig. 2 for the simple-cubic case and in Fig. 3 for the fcc case. In drawing these figures we chose $\alpha=1$, in view of the fact that the energy shift is directly proportional to α and hence shifts of arbitrary α

TABLE II. Values of the calculated dimensionless parameter λ. The ionization energy used in the calculation is 4.32 eV for potassium and 3.87 eV for cesium (Ref. 17). a is the nearest-neighbor distance in Å in KCl, KBr, and KI but represents the lattice constant in Å in CsI.

	KCl	KBr	KI	CsI
a	3.14	3.29	3.53	4.57
$\lambda=\lambda' a$	2.83	2.96	3.18	3.70

TABLE III. Values of $|J|$, and the normalized exciton energy x. For KCl, KBr, and KI, $4|J|$ – the bandwidth in eV – [1 0 0] direction is obtained from Phillips (Ref. 18). For CsI the bandwidths in the [1 0 0] and [1 1 1] directions are obtained from Onodera (Ref. 16) and the average value is used for $|J|$.

	KCl	KBr	KI	CsI
$\lvert J\rvert$	0.83	0.65	0.50	0.32
x	9.4	10.4	11.6	18

can easily be obtained. In general, the polaron band $E_p(\vec{k})$ is lowered when α, x, and λ increase. Furthermore, the shift $\Delta E(\vec{k})$ increases as $\vec{k}$ increases. Thus the polaron band is not merely shifted down from the bare band but its shape is also distorted. The result that the electronic polarization increases as $\vec{k}$ increases can be explained as follows. As $\vec{k}$ increases, the energy of the electron in the bare band increases and thus the electron has a larger probability of creating virtual excitons. In other words, as $\vec{k}$ increases $\langle N\rangle$, the number of virtual excitons surrounding the electron, increases as shown in Fig. 4 and hence $\Delta E(\vec{k}) \propto \langle N\rangle x$ increases. Of course, in accordance with physical intuition if the electron's speed becomes sufficiently large the polarization will start to decrease again. Thus we expect the electronic polarization energy versus the kinetic energy of the electron to increase for small $\vec{k}$ from a constant $\alpha\epsilon$, come to a maximum, and then decrease again.[22] As λ increases a similar effect occurs, the number of excitons again increases (see Fig. 4). Mathematically, this is due to the matrix element describing the electron-exciton interaction

$$V_q^2(0) \propto \left[\int |\phi(r)|^2 e^{i\vec{q}\cdot\vec{r}} d\vec{r}\right]^2 = \left[\frac{16\lambda^4}{(4\lambda^2+q^2)^2}\right]^2 .$$

This matrix element asymptotically approaches 1 from zero as λ increases. Physically, this effect can again be explained from the energy point of view. As λ increases the orbital kinetic energy of the electron increases and its ability to create virtual excitons again increases. The change in conduction-band width in the [100] direction is

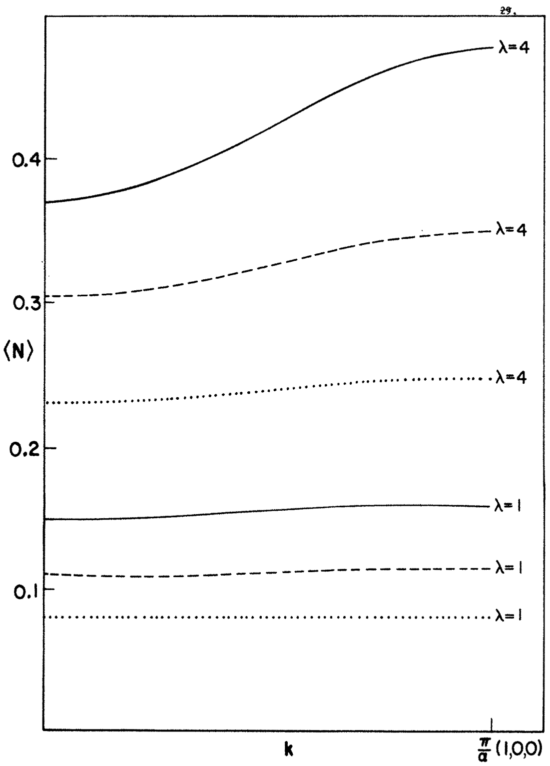

FIG. 4. $\langle N\rangle$ is plotted versus k in the simple cubic case in [1 0 0] direction for $\alpha = 1$. Solid lines refer to $x = 6$, broken to $x = 12$, and dotted to $x = 18$. According to Toyozawa, at $k = 0$, $\langle N\rangle = \frac{1}{2}\alpha$.

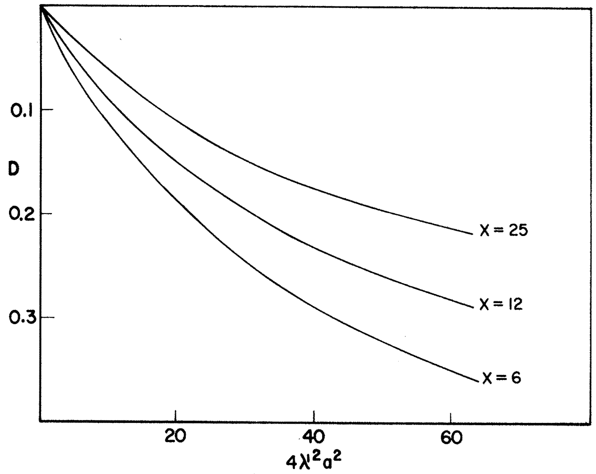

FIG. 5. D versus $4\lambda'^2 a^2$ in [1 0 0] direction in simple-cubic case for $\alpha = 1$. D is the change in bandwidth, in units of $|J|$, caused by the electronic polarization. The bandwidth without polarization is 2.

TABLE IV. Self-energy in eV of an extra electron at the bottom of the conduction band. Row 1 shows the self-energy according to Toyozawa (Ref. 2). Row 2 shows the self-energy for the case in which the atomic nature of the lattice is neglected, the effective-mass approximation is used, and the Brillouin zone is replaced by a sphere of radius π/a. Row 3 shows our results. Row 4 shows the classical results H_{se} of DuPré *et al.* (Ref. 4).

	KCl	KBr	KI	CsI
$\alpha\epsilon$	3.73	3.34	3.53	3.82
$\alpha\epsilon(2/\pi)\tan^{-1}[\pi\hbar/\sqrt{(2m_b\epsilon a^2)}]$	1.94	1.84	1.92	1.74
$\Delta E(0)$	2.75	2.34	2.38	1.68
H_{se}	1.96	2.06	2.18	···

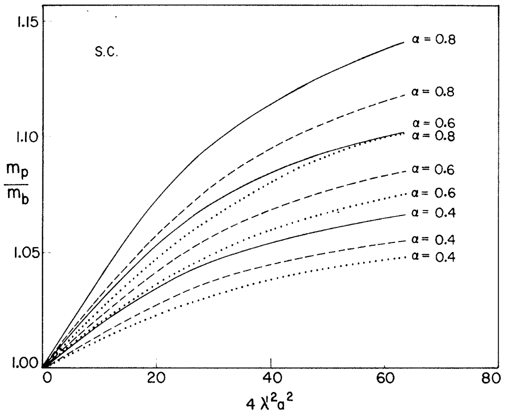

FIG. 6. m_p/m_b versus $4\lambda'^2a^2$ in the simple-cubic case. Solid lines refer to values of $x=6$, broken of $x=12$, dotted of $x=18$.

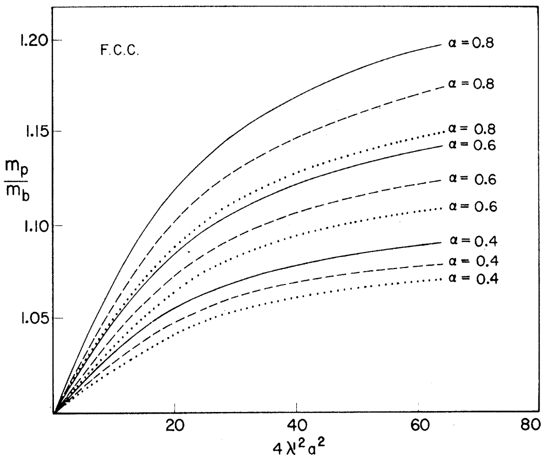

FIG. 7. m_p/m_b versus $4\lambda'^2a^2$ in the fcc case. Solid lines refer to values of $x=6$, broken of $x=12$, dotted of $x=18$.

shown in Fig. 5 as a function of α, x, and λ.

We now discuss the shift at $k=0$. According to Toyozawa,[2] the shift at the bottom of the conduction band is $\alpha\epsilon$. This result can be obtained from our basic equation for the energy shift, i.e., Eq. (22) as discussed in Sec. III A. If we keep the Brillouin zone finite the energy shift in dimensionless units becomes $\alpha x\,(2/\pi)\tan^{-1}(\pi/\sqrt{2x})$ (see Sec. III A), a result which has also been obtained by Fowler.[5] For realistic values of x this latter result reduces the self-energy $\alpha\epsilon$ approximately by a factor of 2. These results, our results obtained by using the parameters given in Tables I–III, in Figs. 2 and 3, and the classical results[6] are summarized in Table IV. In general, the results are of the same order of magnitude so that the essential part of the polarization energy seems to be included in the classical results.

D. Features of Effective Mass

The ratio m_p/m_b versus $4\lambda'^2a^2$ is plotted in Figs. 6 and 7. The general features are the following. As λ' increases, m_p increases more rapidly than m_b (m_b increases since the atoms effectively get further apart). We can expect this result since, according to the discussion in the previous section, as λ' increases the interaction of the excess electron and virtual excitons increases. Also, because there is a stronger interaction, m_p increases as α increases. m_p decreases as x increases since the probability of creating virtual excitons is reduced.

Our results for m_p/m_b agree closely (see Table V) with those of Toyozawa, according to whom $m_p/m_b = 1+\frac{1}{6}\alpha$. Finally, we note that changes in effective mass caused by electronic polarization effects are considerably less important than those due to ionic polarization effects.

TABLE V. Ratio of electronic polaron band mass to bare band mass. Row 1 shows Toyozawa's value (Ref. 2) and row 2 shows ours.

	KCl	KBr	KI	CsI
$m_p/m_b = 1+\frac{1}{6}\alpha$	1.080	1.082	1.096	1.110
m_p/m_b	1.082	1.083	1.108	1.079

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†On leave from Tokyo Metropolitan University, Tokyo, Japan.

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Attempt to Design a Strong Solid*

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It is shown that by using alternate layers of materials with high and low elastic constants resolved shearing stresses of the order of $\mu_{\text{low}}/100$ will be required in order to drive dislocations through the combination. The layers should be so thin that a Frank Read source cannot operate inside one layer. The low-elastic-constant material should be such that perfect dislocations rather than partials occur in bulk specimens of the material. Several possible combinations are suggested.

Present knowledge about dislocations should be enough to suggest methods of preparing specimens which resist deformation and which are not susceptible to brittle fracture. Friedel reviewed the situation.[1]

We would like to propose a composite material which is rather different from previous suggestions. Suppose that a specimen is prepared by epitaxial crystal growth which consists of alternate layers of crystals A and B. We attempt to choose the two crystals such that:

(a) Their lattice parameters, at the operating temperature, are nearly equal. Actually we want to grow the two crystals on one another epitaxially without having large strains present at the interface.

(b) Their thermal expansions should be as nearly equal as possible so that changes in temperature will not destroy the lattice fit at the interfaces.

(c) The elastic constants should differ by as much as possible. What is really required is that the line energy (i.e., the energy per unit length) of the dislocations should be as different as possible in large single crystals of materials A and B. If B is the material associated with large line energy the dislocations prefer to be in A. Moreover a very large external stress will be required to drive dislocations from A into B.

(d) The bonding between A atoms and B atoms should be large, i.e., of the same order as the bonding between two A atoms or between two B atoms.

Note that we did not require that materials A and B have the same crystal structure. In fact, interesting complications probably arise if A and B have different crystal structures.

(e) The thicknesses of the A and B layers must be small. The A layer (i.e., the low-line-energy material) must be thin enough so that dislocation