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The Surface or Interface Polaron in Polar Crystals

II. Strong-Coupling Limit[2])

By

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The effective Hamiltonian and effective potential are given for the surface strong coupling polaron in polar crystals. Their binding energy and effective mass are also evaluated. When a piece of a polar crystal contacts with a piece of another non-polar material, and the high frequency dielectric constant $\varepsilon_{\infty 2}$ of the non-polar material is larger than that (i.e. $\varepsilon_{\infty 1}$) of the polar crystal, or is larger than a certain critical value $(\varepsilon_{\infty 2})_{\min}$, polarons can exist in the interface. Reversely, when $\varepsilon_{\infty 2} < (\varepsilon_{\infty 2})_{\min}$, the polaron is not able to exist near the interface. If the non-polar material is metallic (i.e. $\varepsilon_{\infty 2} = \infty$), there is a deeper potential well near the interface in which the polaron may be trapped.

Представляется эффективный Гамильтон и эффективный потенциал, которые принадлежат поверхностному полярону сильной связи в поляроных кирсталлах. Вычислены их энергия связи и эффективная масса. Возможно существовать поляроны на границе раздела, когда полярный кристалл соприкасается с другим неполярным материалом, и безынерционных диэлектрических проницаемостей $\varepsilon_{\infty 2}$ неполярных материалов больше, чем $\varepsilon_{\infty 1}$ полярных кристаллов, или $\varepsilon_{\infty 2}$ больше, чем некоторых критических значений $(\varepsilon_{\infty 2})_{\min}$. И напротив, поляроны не могут образовать на границе, при $\varepsilon_{\infty 2} < (\varepsilon_{\infty 2})_{\min}$. Если неполярный материал является металлом ($\varepsilon_{\infty 2} = = \infty$), то появляется грубокая потенциальная яма, в которой возможно ловить поляроны.

1. The Strong-Coupling Limit

In the previous paper [1], I have derived the expression of the expectation value of $(U_1U_2)^{-1}(H - \boldsymbol{u}_{\|} \cdot \boldsymbol{P}_{\|T})(U_1U_2)$ for the surface polaron (henceforward, I will denote the results oft he previous paper as I). They are, in principle, usable for arbitrary coupling strength. However, as there is anunknown parameter A characterizing the coupling strength in this expression, we can obtain some useful results only for the strong-coupling and weak-coupling limits. In the previous paper, we have accounted for the weak-coupling limit, the case of $A = 1$. Now, I will account for the case of $A = 0$ which corresponds to the strong-coupling limit. Then, putting $A = 0$ in (I, 15), we have

$$\begin{aligned} F(f_Q, f_q, f_Q^*, f_q^*, \boldsymbol{p}_0, \boldsymbol{u}_{\|}, \lambda) &= \langle 0| H_2^{(0)} - \boldsymbol{u}_{\|} \cdot \boldsymbol{P}_2 |0\rangle = \\ &= \frac{\hbar\lambda}{2} + \frac{\hbar\lambda}{4} p_0^2 + \frac{p_z^2}{2m_z^*} + \frac{e^2}{4z} \frac{(\varepsilon_{\infty 1} - \varepsilon_{\infty 2})}{\varepsilon_{\infty 1}(\varepsilon_{\infty 1} + \varepsilon_{\infty 2})} - \left(\frac{m_{\|}^*\hbar\lambda}{2}\right)^{1/2} \boldsymbol{u} \cdot \boldsymbol{p}_0 + \\ &+ \sum_{\boldsymbol{Q}} (\hbar\omega_s - \hbar\boldsymbol{u}_{\|} \cdot \boldsymbol{Q}) |f_Q|^2 + \sum_{\boldsymbol{q}} (\hbar\omega_0 - \hbar\boldsymbol{u}_{\|} \cdot \boldsymbol{q}_{\|}) |f_q|^2 + \\ &+ \sum_{\boldsymbol{Q}} \left\{ V_Q^* f_Q^* \exp\left(-\frac{\hbar}{4m_{\|}^*\lambda} Q^2 - Qz\right) + \text{c.c.}\right\} + \\ &+ \sum_{\boldsymbol{q}} \left\{ V_q^* f_q^* \exp\left(-\frac{\hbar}{4m_{\|}^*\lambda} q^2\right) \sin(q_z z) + \text{c.c.}\right\}, \end{aligned} \tag{1}$$

[1]) Changchun, Jilin, The People's Republic of China.

[2]) Part I see phys. stat. sol. (b) 127, 307 (1985).

where $H_2^{(0)}$ and P_2 are the new Hamiltonian and momentum obtained after twice unitary transformation which are $(U_1U_2)^{-1} H(U_1U_2)$ and $(U_1U_2)^{-1} \boldsymbol{P}_{||T} (U_1U_2)$ in (I.11) and (I.1,3) respectively. $\boldsymbol{u}_{||}$ is the Lagrange's multiplier, f_Q, f_q and their complex conjugate forms are the variational functions, $\boldsymbol{p}_0$ and λ the variational parameters. In addition, V_Q and V_q are the coupling strength coefficients which are also given in (I.2) and (I.3).

Minimizing (1) with respect to f_Q, f_q, ..., we can obtain these functions. Inserting these functions into (1), F becomes

$$F(\boldsymbol{p}_0, \boldsymbol{u}_{||}, \lambda) = \frac{\hbar\lambda}{2} + \frac{\hbar\lambda}{4} p_0^2 - \frac{m_{||}^*\hbar\lambda}{2} \boldsymbol{u}_{||}\cdot\boldsymbol{p}_0 - \frac{p_z^2}{2m_z^*} + \frac{e^2}{4z}\frac{(\varepsilon_{\infty1}-\varepsilon_{\infty2})}{\varepsilon_{\infty1}(\varepsilon_{\infty1}+\varepsilon_{\infty2})} -$$
$$- \sum_{\boldsymbol{Q}} \frac{|V_Q|^2}{\hbar\omega_s}\left[1 + \hbar^2\left(\frac{\boldsymbol{u}_{||}\cdot\boldsymbol{Q}}{\hbar\omega_s}\right)^2\right]\exp\left[-\frac{\hbar}{2m_{||}^*\lambda}Q^2 - 2Qz\right] -$$
$$- \sum_{\boldsymbol{q}} \frac{|V_q|^2}{\hbar\omega_0}\left[1 + \hbar^2\left(\frac{\boldsymbol{u}_{||}\cdot\boldsymbol{q}_{||}}{\hbar\omega_0}\right)^2\right]\exp\left[\frac{\hbar}{2m_{||}^*\lambda}q^2\right]\sin(q_z z)\,, \qquad (2)$$

where we have expanded $[1-(\boldsymbol{u}_{||}\cdot\boldsymbol{q}_{||}/\omega_0)]^{-n}$ and $[1-(\boldsymbol{u}_{||}\cdot\boldsymbol{Q}/\omega_s)]^{-n}$ contained in f_Q, f_q and their square expressions ($n = 1$ or 2) in the series of $\boldsymbol{u}_{||}\cdot\boldsymbol{Q}$ and $\boldsymbol{u}_{||}\cdot\boldsymbol{q}_{||}$, and only the second-order terms are retained. Carrying out the variation of (2) with respect to $\boldsymbol{p}_0$ gives

$$\boldsymbol{p}_0 = \left(\frac{2m_{||}^*}{\hbar\lambda}\right)^{1/2}\boldsymbol{u}_{||}\,. \qquad (3)$$

Inserting this $\boldsymbol{p}_0$ into (2) and changing the summation over $\boldsymbol{Q}$ and $\boldsymbol{q}$ to integration, we finally have

$$F(u,\lambda) = \frac{\hbar\lambda}{2} - \frac{1}{2}m_{||}^*u_{||}^2 + \frac{p_z^2}{2m_z^*} + \frac{e^2}{4z}\frac{(\varepsilon_{\infty1}-\varepsilon_{\infty2})}{\varepsilon_{\infty1}(\varepsilon_{\infty1}+\varepsilon_{\infty2})} -$$
$$- \frac{\sqrt{\pi}\,\alpha\hbar\omega_0}{4}\left(\frac{m_{||}^*\bar{\lambda}}{m^*}\right)^{1/2} - \frac{\alpha\hbar\omega_0}{\sqrt{\pi}}\left(\frac{m_{||}^*\bar{\lambda}}{m^*}\right)^{1/2}\left(A_1 - \frac{1}{2}\right)f_1(z) -$$
$$- \frac{\sqrt{\pi}\,\alpha m_{||}^*u_{||}^2}{8}\left(\frac{m_{||}^*}{m^*}\right)^{1/2}(\bar{\lambda})^{3/2} - \frac{\alpha\hbar u_{||}^2}{2\beta_0\omega_0}\left[A_1\left(\frac{\omega_0}{\omega_s}\right)^2 - \frac{1}{2}\right]f_2(z)\,. \qquad (4)$$

Here we have put $\bar{\lambda} = (\lambda/\omega_0)$,

$$A_1 = \frac{2\varepsilon_0\varepsilon_{\infty1}}{(\varepsilon_0+1)(\varepsilon_{\infty1}+1)}\,, \qquad (5)$$

$$f_1(z) = \int_0^\infty \frac{\exp[-(2m_{||}^*\omega_0\bar{\lambda}/\hbar)z^2x^2]}{1+x^2}\,dx\,, \qquad (6)$$

$$f_2(z) = \int_0^\infty x^2\exp\left(-\frac{\hbar}{2m_{||}^*\omega_0\bar{\lambda}}x^2 - 2zx\right)dx\,. \qquad (7)$$

$|V_Q|^2$ and $|V_q|^2$ have been replaced by the values given in (I.2) and (I.3). (4) does not contain terms of odd order in $\boldsymbol{Q}$ and $\boldsymbol{q}$, because these terms vanish in integrating over $\boldsymbol{Q}$ and $\boldsymbol{q}$. It is evident from (4) that, as $\bar{\lambda}$ occurs in the error function, it is quite difficult to get an analytic experession for it. If we take $z(2m^*\omega_0\bar{\lambda}/\hbar)^{1/2} \gg 1$ and $z(2m^* \times \omega_0\bar{\lambda}/\hbar)^{1/2} \ll 1$ as two extremum cases, the problem may be greatly simplified and an approximate expression for $\bar{\lambda}$ can be also obtained. However, this will result in the region of $z \sim (2m^*\omega_0\bar{\lambda}/\hbar)^{1/2}$ which is most important for the surface polarons out of account, so we will apply the iteration method instead.

In the variation of (4) with respect to $\bar{\lambda}$, we assume that the contribution of the terms containing $u_{||}^2$ can be ignored and $\bar{\lambda}$ in the integrand of $f_1(z)$ may be regarded as a constant $\bar{\lambda}_c$. Performing the variation of (4) with respect to $\bar{\lambda}$, we get

$$\bar{\lambda}^{1/2} = \left(\frac{\lambda}{\omega_c}\right)^{1/2} = \frac{\sqrt{\pi}\,\alpha}{4}\left(\frac{m_{||}^*}{m^*}\right)^{1/2}\left\{1 + \frac{4}{\pi}\left[A_1 - \frac{1}{2}\right] f_1(z)\right\}. \tag{8}$$

$\bar{\lambda}_0$ may be regarded as a value of the zero-order approximation, or, if necessary, may be also considered as a value of the first-order approximation. If $\bar{\lambda}_c$ in $f_1(z)$ is taken to be a zero-order value, i.e. $\bar{\lambda}_0 = (\pi\alpha^2 m_{||}^*/16m^*)^{1/2}$, $\bar{\lambda}_0$ determined from (8) is a first-order value.

Inserting all the variational functions and parameters determined above into (I.13), the expectation value of $\boldsymbol{P}_2$ for the ground state $|0\rangle$ is obtained to be (henceforth, denoted by $\mathscr{P}_{||}$)

$$\mathscr{P}_{||} = m_{||}^*\left\{1 + \frac{\sqrt{\pi}}{4}\left(\frac{m_{||}^*}{m^*}\right)^{1/2}(\bar{\lambda})^{3/2}\alpha + \frac{\alpha\hbar}{\beta_0\omega_0 m_{||}^*}\left[A_1\left(\frac{\omega_0}{\omega_s}\right)^2 - \frac{1}{2}\right] f_2(z)\right\}\boldsymbol{u}_{||}\,. \tag{9}$$

It is evident from (9) that the factor before $\boldsymbol{u}_{||}$

$$M_{\text{eff}}^* = m_{||}^*\left\{1 + \frac{\sqrt{\pi}}{4}\left(\frac{m_{||}^*}{m^*}\right)^{1/2}(\bar{\lambda})^{3/2}\alpha + \frac{\alpha\hbar}{\beta_0\omega_0 m_{||}^*}\left[A_1\left(\frac{\omega_0}{\omega_s}\right)^2 - \frac{1}{2}\right] f_2(z)\right\} \tag{10}$$

can be interpreted as the effective mass of the polaron, and $\boldsymbol{u}_{||}$ has the meaning of the velocity which can be interpreted as the translation velocity of the polaron in the xy plane.

Similarly, inserting these variational functions and parameters determined above into (I.11), the expectation value of $H_2^{(0)}$ for the ground state $|0\rangle$ is obtained to be (hence-forth, denoted by H_{eff})

$$H_{\text{eff}} = \frac{p_z^2}{2m_z^*} + \frac{\mathscr{P}_{||}^2}{2M_{\text{eff}}^*} + \frac{e^2}{4z}\frac{(\varepsilon_{\infty1} - \varepsilon_{\infty2})}{\varepsilon_{\infty1}(\varepsilon_{\infty1} + \varepsilon_{\infty2})} - \frac{\pi\alpha^2}{32}\left(\frac{m_{||}^*}{m^*}\right)\left\{1 + \frac{4}{\pi}\left[A_1 - \frac{1}{2}\right] f_1(z)\right\}^2. \tag{11}$$

It may be called the effective Hamiltonian. An inspection of (11) shows that the first term represents the kinetic energy of the polaron for the motion in z-direction and the rest of the terms, namely,

$$\begin{aligned} V_{\text{eff}} = {} & \frac{\mathscr{P}_{||}^2}{2M_{\text{eff}}^*} + \frac{e^2}{4z}\frac{(\varepsilon_{\infty1} - \varepsilon_{\infty2})}{\varepsilon_{\infty1}(\varepsilon_{\infty1} + \varepsilon_{\infty2})} - \\ & - \frac{\pi}{32}\alpha^2\hbar\omega_0\left(\frac{m_{||}^*}{m^*}\right)\left\{1 + \frac{4}{\pi}\left[\frac{2\varepsilon_0\varepsilon_{\infty1}}{(\varepsilon_1 + 1)(\varepsilon_{\infty1} + 1)} - \frac{1}{2}\right] f_1(z)\right\}^2, \end{aligned} \tag{12}$$

can be interpreted as effective potential function for the motion in z-direction.

Taking the expectation value of the effective Hamiltonian (11) with respect to ψ_z the ground state energy E_0 is obtained to be

$$\begin{aligned} E_0 &= \langle\psi_z|\, H_{\text{eff}}\, |\psi_z\rangle \\ &= \frac{\mathscr{P}_{||}^2}{2M_{\text{eff}}^*} + \langle\psi_z|\,\frac{p_z^2}{2m_z^*} + \frac{e^2}{4z}\,\frac{(\varepsilon_{\infty1} - \varepsilon_{\infty2})}{\varepsilon_{\infty1}(\varepsilon_{\infty1} + \varepsilon_{\infty2})}\,|\psi_z\rangle - \\ &\quad - \frac{\pi}{32}\alpha^2\hbar\omega_0\left(\frac{m_{||}^*}{m^*}\right)\langle\psi_z|\left\{1 + \frac{4}{\pi}\left[\frac{2\varepsilon_0\varepsilon_{\infty1}}{(\varepsilon_0 + 1)(\varepsilon_{\infty1} + 1)} - \frac{1}{2}\right] f_1(z)\right\}^2 |\psi_z\rangle\,. \end{aligned} \tag{13a}$$

2. The Calculations and Discussions

Since there is an unknown quantity $\bar{\lambda}$ in the expressions of the ground state energy, effective potential, and effective mass, first we must determine which value it takes. For this purpose, we inspect carefully the integral (6). It may be rewritten as

$$f_1(z) = \pi^{1/2} \int_{b^{1/2}z}^{\infty} \exp\left[-(x - b^{1/2}z)\,(x + b^{1/2}z)\right] \mathrm{d}x; \qquad b^{1/2} = \left(\frac{2m_{\|}^{*}\omega_0\bar{\lambda}}{\hbar}\right)^{1/2}.$$

Evidently, this integral has a maximum at $x = b^{1/2}z$. On the other hand, (6) can also be represented as (making use of the integration by parts)

$$f_2(z) = 2\pi^{1/2} \int^{\infty} x(x - b^{1/2}z) \exp\left[-(x - b^{1/2}z)\,(x + b^{1/2}z)\right] \mathrm{d}x$$

Comparing (15b) and (15c), one can see that there is a formal resemblance between these two expressions, only their numerical values differ a little. Therefore, we may safely assume that $\langle \bar{\lambda}^{1/2} \rangle$ as given by (15c) is applicable to the whole region of $z > 0$. Making use of the trial function (16) and inserting $\langle \bar{\lambda}^{1/2} \rangle$ represented by (15c) into (13a), after some simple calculations we find the ground state energy to be (putting $(m_{||}^*/m^*) = 1$)

$$E_0 = \frac{\mathscr{P}_{||}^{*}}{2M_{\text{eff}}^*} + \zeta'^2 \hbar\omega_0 + \frac{\varepsilon_0(\varepsilon_{\infty 1} - \varepsilon_{\infty 2})}{2(\varepsilon_0 - \varepsilon_{\infty 1})(\varepsilon_{\infty 1} + \varepsilon_{\infty 2})} \zeta' \alpha \hbar\omega_0 - \frac{\pi}{32} \alpha^2 \hbar\omega_0 -$$
$$- \frac{1}{2} \hbar\omega_0 \left\{ \left(A_1 - \frac{1}{2}\right) \alpha \left[1 + \frac{8}{\pi}\left(A_1 - \frac{1}{2}\right)\frac{\zeta'}{\alpha}\right]^{-1} + \right.$$
$$\left. + \frac{8}{\pi}\left(A_1 - \frac{1}{2}\right)^2 \left[1 + \frac{8}{\pi}\left(A_1 - \frac{1}{2}\right)\frac{\zeta'}{\alpha}\right]^{-2} \zeta'^2 \right\}. \tag{13b}$$

Here we have used $\beta_0 = (2m^*\omega_0/\hbar)^{1/2}$ as a unit of length, i.e. $\zeta' = \zeta/\beta_0$. For convenience of writing, let us put

$$A_2 = \frac{\varepsilon_0(\varepsilon_{\infty 1} - \varepsilon_{\infty 2})}{(\varepsilon_0 - \varepsilon_{\infty 1})(\varepsilon_{\infty 1} + \varepsilon_{\infty 2})}. \tag{17}$$

Then, the extremum condition for the ground state energy, $(\partial E_c/\partial \zeta') = 0$, gives

$$\left(2\zeta' + \frac{\alpha}{2} A_2\right)\left[1 + \frac{8}{\pi}\left(A_1 - \frac{1}{2}\right)\frac{\zeta'}{\alpha}\right]^3 - \frac{1}{2}\alpha\left(A_1 - \frac{1}{2}\right)\left[1 + \frac{8}{\pi}\left(A_1 - \frac{1}{2}\right)\frac{\zeta'}{\alpha}\right]^2 -$$
$$- \frac{4}{\pi}\left(A_1 - \frac{1}{2}\right)^2\left[1 - \frac{8}{\pi}\left(A_1 - \frac{1}{2}\right)\frac{\zeta'}{\alpha}\right] = 0\,. \tag{18}$$

From this equation ζ' can be found. But the last term in the above equation is small compared with the other terms. If we ignore it, an approximate analytic expression for ζ' can be obtained,

$$\zeta' = \alpha \times$$
$$\times \frac{-\left[A_2\left(A_1 - \frac{1}{2}\right) + \frac{\pi}{2}\right] + \left\{\left[A_2\left(A_1 - \frac{1}{2}\right) + \frac{\pi}{2}\right]^2 - 2\pi\left(A_1 - \frac{1}{2}\right)\left[A_2 - \left(A_1 - \frac{1}{2}\right)\right]\right\}^{1/2}}{4\left(A_1 - \frac{1}{2}\right)}. \tag{19}$$

ζ' has the meaning of the reverse state radius of the surface polaron. Evidently, ζ' cannot be smaller than zero, or else it will lose its meaning. It means that the interface polaron can be formed only in satisfying the following condition:

$$A_2 - (A_1 - \tfrac{1}{2}) < 0\,. \tag{20}$$

In fact, this condition can be satisfied as long as $\varepsilon_{\infty 2}$ is larger than a certain critical value $(\varepsilon_{\infty 2})_{\min}$. From (20) and (17) this critical value is given by

$$(\varepsilon_{\infty 2})_{\min} = \frac{\varepsilon_{\infty 1}[\varepsilon_0 - (\varepsilon_0 - \varepsilon_{\infty 1})(A_1 - \frac{1}{2})]}{\varepsilon_0 + (\varepsilon_0 - \varepsilon_{\infty 1})(A_1 - \frac{1}{2})}. \tag{21}$$

This $(\varepsilon_{\infty 2})_{\min}$ is also the critical value for the dead layer of the polarons, i.e. when $\varepsilon_{\infty 2} < (\varepsilon_{\infty 2})_{\min}$, polarons cannot exist near the interface.

Substituting (19) into (13b), we finally obtain

$$E_0 = \frac{\mathscr{P}_{\parallel}^2}{2M_{\text{eff}}^*} - \frac{\pi}{32}\alpha^2 - \frac{\alpha^2}{16}\left\{\frac{\pi B^2}{(\pi + B)^2} + \frac{\pi B}{(\pi + B)} - \frac{B^2}{4(A_1 - \frac{1}{2})} - \frac{A_2 B}{(A_1 - \frac{1}{2})}\right\}, \tag{22}$$

where we have used $\hbar\omega_0$ as energy unit and

$$B = -\left[A_2\left(A_1 - \frac{1}{2}\right) + \frac{\pi}{2}\right] + \left\{\left[A_2\left(A_1 - \frac{1}{2}\right) + \frac{\pi}{2}\right] - 2\pi\left(A_1 - \frac{1}{2}\right)\left[A_2 - \left(A_1 - \frac{1}{2}\right)\right]\right\}^{1/2}. \tag{23}$$

From the above results we come to the conclusion that the ground state energy of the interface polaron is as that of the bulk polaron proportional to α^2, but its value is much larger than that of the bulk polaron. In general, the binding energy of the surface polaron is defined as the difference of the ground state energy of surface polaron and bulk polaron. Taking the ground state energy of the bulk polaron as $(\alpha^2/3\pi)$, and taking the average kinetic energy of the surface polaron parallel to the xy plane as zero, the binding energy of the interface polaron is

$$\Delta E_0 = \frac{\pi}{32}\alpha^2 - \frac{1}{3\pi}\alpha^2 + \frac{1}{16}\alpha^2 B^2\left\{\frac{\pi}{(\pi + B)^2} - \frac{1}{4(A_1 - \frac{1}{2})^2}\right\} + \frac{1}{16}\alpha^2 B\left\{\frac{\pi}{(\pi + B)} - \frac{A_2}{(A_1 - \frac{1}{2})}\right\}. \tag{24}$$

The values of ζ' and ΔE calculated from (19) and (24) for some alkali halides and cuprous oxide (Cu_2O) are given in Table 1.

Now, we return to discuss the effective potential of the polarons. Because the image potential is inversely proportional to z (the distance from the interface), it is evident from the effective potential (12) that when $\varepsilon_{\infty 2} < \varepsilon_{\infty 1}$, or $\varepsilon_{\infty 2}$ is smaller than a critical value $(\varepsilon_{\infty 2})_{\min}$, the effective potential may be a positive value within a certain z range. In this case there is no polaron near the surface which is called the dead layer for the polaron. As we pointed out in the previous paper, we can assume that the effect of the kinetic energy will decrease the polarization potential energy 1/4 of its original value [5]. Then, from (12) we have the equation determining the thickness of the dead layer which is given by (putting $(m_{\parallel}^*/m^*) = 1$)

$$\frac{3\pi}{64}\alpha\left\{1 + \frac{4}{\pi}\left(A_1 - \frac{1}{2}\right) f_1(z)\right\}^2 z' - \frac{\varepsilon_0(\varepsilon_{\infty 1} - \varepsilon_{\infty 2})}{(\varepsilon_0 - \varepsilon_{\infty 1})(\varepsilon_{\infty 1} + \varepsilon_{\infty 2})} = 0\,, \tag{25}$$

where $z' = \beta_0 z$, and $f_1(z)$ is approximately given by (14), but in which $\bar{\lambda}$ is replaced by the value given in (15a). After some simple calculations, (25) becomes

$$\tfrac{3}{64}[\pi\alpha z' + 8(A_1 - \tfrac{1}{2})]^3 + [\tfrac{3}{8}(A_1 - \tfrac{1}{2}) - A_2][\pi\alpha z' + 8(A_1 - \tfrac{1}{2})]^2 - 3(A_1 - \tfrac{1}{2})^2[\pi\alpha z' + 8(A_1 - \tfrac{1}{2})] - 24(A_1 - \tfrac{1}{2})^3 = 0\,. \tag{26a}$$

The calculation shows that when the polar crystal is in contact with vacuum, i.e. $\varepsilon_{\infty 2} = 1$, the polaron cannot exist within a certain range near the interface. The thick-

Table 1

The calculated values of the dead layer z_0, binding energies ΔE_0 and the reverse state radius ζ' for the interface polarons*)

	m^* (m_0)	α_0	ω_0 ($10^{13}\,s^{-1}$)	ε_0	$\varepsilon_{\infty 1}$	$\varepsilon_{\infty 2}$	z_0 (10^{-10} m) from (26a)	(26b)	ΔE_0 ($\hbar\omega_0$)	ζ' (β_0)
						1	0.35	0.56		
NaCl	2.78	5.5	4.9	5.26	2.25	2.0			0.927	1.7
									24.53	4.65
						1	0.85	1.05		
KCl	1.85	5.6	3.87	4.68	2.13	2.0			0.607	0.89
									19.04	4.13
						1	0.73	0.73		
NaBr	2.96	5.0	3.84	5.99	2.62	2.3			1.014	1.05
									24.33	4.61
						1	0.87	0.75		
NaI	3.25	4.8	3.31	6.6	2.91	2.5			1.158	1.08
									25.36	4.68
						1	2.7			
KI	2.11	4.6	2.76	4.94	2.69	2.3			0.381	0.71
									19.94	4.61
						1	1.7			
Cu_2O	1.81	2.5	8.1	10.5	4.0	3.0			0.213	0.42
									3.53	1.71

*) The values of m^*, α_0, ω_0, ε_0 and $\varepsilon_{\infty 1}$ are taken from [4]. m_0 is the mass of the free electron, α_0 the Fröhlich constant for $m^* = 1$.

nesses of the dead layer calculated from (26a) for some alkali halides and cuprous oxide (Cu_2O) are given in Table 1. One can see from this table that the thicknesses of the dead layer are rather small for these materials. They are about 0.1 nm. However, as the values of z are small, if we put $z = 0$ in $f_1(z)$, from (25) we can easily obtain

$$z = \frac{16A_2}{3\pi\alpha A_1^2}. \tag{26b}$$

For comparison, the values calculated from (26b) for some alkali halides are also given in Table 1. It is shown that the thicknesses of the dead layer obtained from (26a) and (26b) are nearly consistent.

Reversely, when the high frequency dielectric constant $\varepsilon_{\infty 2}$ of the non-polar material is larger than $\varepsilon_{\infty 1}$, or larger than a certain critical value $(\varepsilon_{\infty 2})_{\min}$, according to (12), the effective potential of the polaron is negative. In this case, the polarons can be trapped near the interface. Let us assume that the non-polar material contacted with a piece of polar crystal is a metal, i.e. $\varepsilon_{\infty 2} = \infty$, substituting (15a) into $f_1(z)$ of (12), we have

$$V_{\text{eff}} = \frac{\mathcal{P}_\parallel^2}{2M_{\text{eff}}^*} - \frac{e^2}{4\varepsilon_{\infty 1} z} - \frac{\pi}{32}\alpha^2\hbar\omega_0\left\{1 + \frac{8(A_1 - \frac{1}{2})}{\pi\alpha\beta_0 z + 8(A_1 - \frac{1}{2})}\right\}^2. \tag{27}$$

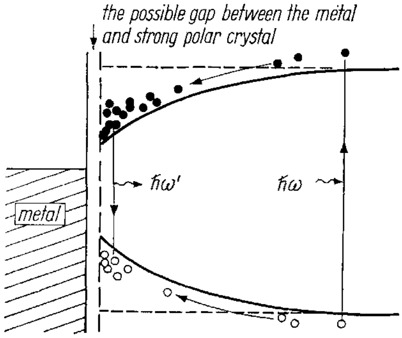

Fig. 1. The potential well for the electron polarons and hole polarons near the interface of a metal and a strong polar crystal, ● the electron polaron, ○ the hole polaron

Fig. 1 shows the typical behaviour of this potential function near the interface. The upper and lower branches in this graph are the potential energies of the electron polarons and the hole polarons, respectively. This graph shows that near the interface there exist two kinds of potential well in which the electron polarons and the hole polarons, respectively, can be trapped. It is worth mentioning that the potential wells for the electron polaron and the hole polaron are completely dipped by themselves. They exist with the polarons and disappear with them.

In the polar crystal contacted with metal, if the electrons are excited from the valence band to the conduction band by a radiation with apposite wavelength, under the action of the surface potential, the electrons and holes have a strong tendency to move towards the interface. Recombinations between the electron polarons and hole polarons are also possible to happen near the interface. Since the sum of the depth of both the potential wells is much larger than the binding energy of the bulk polaron and the bulk exciton, the position of the radiative spectrum line emitted at the recombination between them is on the long-wave side of the absorption band and the bulk exciton line. If such radiation can be observed (I think, it should be observed), this phenomenon possibly provides a method for investigating the surface or the interface properties and the behaviour of the polarons near the interface.

Finally, we examine the effective mass of the surface polaron. However, it is difficult to calculate the function $f_2(z)$ in the expression of the effective mass. We can only approximately evaluate it. For the case of $z < 0.1$ nm we may simply take $z \to 0$ in $f_2(z)$, then from (10) we have

$$M^*_{\text{eff}} = m^*_{\|} \left\{1 + \frac{\sqrt{\pi}}{2} \left(\frac{m^*_{\|}}{m^*}\right)^{1/2} A_1 \left(\frac{\omega_0}{\omega_s}\right)^2 (\bar{\lambda})^{3/2} \alpha\right\}.$$

Inserting $\bar{\lambda}^{1/2}$ denoted by (15b) into the above expression gives

$$M^*_{\text{eff}} = m^*_{\|} \left\{1 + \frac{\pi^2}{16} \left(\frac{m^*_{\|}}{m^*}\right)^2 A_1^4 \left(\frac{\omega_0}{\omega_s}\right)^2 \alpha^4\right\}. \tag{28}$$

Reservely, in the case of $z > 0.1$ nm from (7) $f_2(z)$ may be approximately expressed as

$$f_2(z) = \frac{1}{4z} \left(\frac{m^*_{\|}}{m^*}\right) \beta_0^2 \bar{\lambda}.$$

Inserting this result into (10) and averaging it over z gives

$$M^*_{\text{eff}} = m^*_{\|} \left\{1 + \frac{\sqrt{\pi}}{4} \left(\frac{m^*_{\|}}{m^*}\right)^{1/2} \bar{\lambda}^{3/2} \alpha + \frac{1}{2} \zeta' \bar{\lambda} \left[A_1 \left(\frac{\omega_0}{\omega_s}\right)^2 - \frac{1}{2}\right] \alpha\right\}.$$

Inserting $\bar{\lambda}$ given in (15c) and ζ' given in (19) into the above expression, we finally obtain (putting $(m_{||}^*/m^*) = 1$)

$$M_{\text{eff}}^* = m_{||}^* \left\{1 + \frac{\alpha^4}{128} (\pi + 2B)^2 \left[\frac{1}{2} (\pi + 2B) + B \frac{A_1(\omega_s/\omega_0)^2 - (\frac{1}{2})}{(A_1 - \frac{1}{2})}\right]\right\}. \quad (29)$$

Thus, we come to the conclusion that the effective mass of the interface polaron is as that of the bulk polaron proportional to α^4, but its value is much larger than that of the bulk polaron.

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