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Surface-polaron first-order phase-transition-like behavior

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A simple unitary-transformation formalism, successfully applied to the bulk polaron problem, is used in order to investigate the ground-state properties of an electron near a surface of a semi-infinite material and interacting with the surface optical modes. The method has the advantage of being applicable to the whole range of the electron—surface-phonon coupling. A first-order phase-transition—like behavior from the quasifree to the self-trapping electron state as the coupling constant exceeds a certain critical value is observed. The characteristic features of this phase transition such as rapid changes of the ground-state energy, the effective mass, the mean number of surface phonons in the cloud around the electron, and the spatial localization of the electron perpendicular to the surface at the critical coupling constant, are seen. In the present calculation, the coupling of the electron to the bulk excitation modes is not treated.

I. INTRODUCTION

The possibility of an electron to form a bound state, in which it becomes trapped near the surface of a semi-infinite material by virtue of the electron—surface-optical-phonon interaction, has been the subject of renewed interest in recent years.[1–6] The case where an electron interacts with the surface plasmon has proved to be a reasonable model in describing the positron surface states on simple metals.[7,8] In addition, the electron localization in inversion layers in Si has also been studied in terms of the electron—surface-acoustic-phonon interaction model.[9]

Investigations into the surface-polaron ground state have been presented in the weak- and intermediate-coupling constant limits by Evans and Mills[3] using a Lee-Low-Pines[10] variational procedure and at almost the same time by Sak[4] in terms of perturbation theory. The strong-coupling interaction limit, on the other hand, was also worked out by Sak[4] within the product anzatz of Pekar.[11]

In order to evaluate the ground-state energy and the effective mass of the surface polaron over the entire range of the coupling constant, Clark[12] used a variational formalism applied earlier by Larsen[13] to the problem of a bulk polaron trapped in a Coulomb potential. He found a discontinuous change in the slope of the ground-state energy curve as the coupling constant exceeds a certain critical value. This discontinuity has the characteristics of a first-order phase transition in which the surface polaron transforms from a mobile state to a self-trapped state.

Recently, two different approaches, namely, the Feynman path-integral formalism and a modified variational scheme of the Lee-Low-Pines theory, have been applied, respectively, by Huybrechts[14] and Hipólito[15] to investigate the surface-polaron ground state for the entire range of the coupling constant. However, these calculations have not explicitly presented such a phase transition between a nearly-free and self-trapping electron. Farias, Studart, and Hipólito,[1] on the other hand, using a formalism based on a generalized path-integral method applied to the bulk polaron by Luttinger and Lu,[16] have shown the existence of the discontinuity phenomenon at a critical value of the coupling constant. Whether or not the surface-polaron phase transition is merely a consequence of the approximations that were made rather than a property of the general type is still an unanswered question.

Over the last few years, many authors[16–21] conjectured about the existence of a phase transition of bulk polarons. Toyozawa[17] first pointed out that the phase transition is caused by the short-range nature of the interaction between the electron and the phonon but not by the long-range interaction potential. In such a way only the acoustic polaron, in which the interaction between electron and acoustic phonon is of short range, undergoes a phase transition. Later, several investigations into the polaron ground state described the phase transition in terms of the spontaneous symmetry-breaking methods. The po-

laron ground-state wave function is postulated to be the product of a function of electron coordinate only and the coherent virtual-phonon state. This polaron state does not preserve the translational invariance of the Hamiltonian. In such a symmetry-breaking situation the polaron ground state has lower symmetry than the total Hamiltonian. This leads to a phase transition from a nearly-free-polaron state to a self-trapped one.

As was pointed out by Toyozawa,[17] "the word self-trapped should not be taken so literally and the problem of the possibility of the self-trapping should be replaced by the discussion of the magnitudes of the effective mass of this polaron."

The purpose of this paper is to investigate the surface-polaron ground state based on a variational formalism recently proposed by Huybrechts.[22] This method, which is valid for the whole range of the coupling constant, has been successfully applied to the study of the phase-transition-like behavior of different types of bulk polarons by Shoji and Tokuda.[21] We have adapted this formalism to evaluate the ground-state energy, the effective mass, the mean number of surface phonons in the cloud around the electron, and the spatial localization of the electron perpendicular to the surface as functions of the electron–surface-phonon coupling constant. We have considered the case when the electron lies entirely outside the material, which corresponds to neglecting the effect of coupling of the electron to the bulk phonons. It will be shown that a first-order phase-transition behavior will occur at a certain critical value of the coupling constant.

The outline of this paper is as follows. In Sec. II we define the model Hamiltonian for the surface optical polaron. The general expressions for the ground-state energy, effective mass, the mean number of surface phonons in the cloud around the electron, and the spatial localization of the electron perpendicular to the surface are obtained within a variational formalism. In Sec. III we have applied the model for the two cases where the electron is localized at a given distance near the surface and when the electron wave function perpendicular to the surface penetrates the crystal. The numerical results revealing the phase-transition behavior in both cases are discussed. Finally, some concluding remarks are presented in Sec. IV.

II. THE VARIATIONAL MODEL

Let us consider an electron having charge e, free mass m, and band-structure effective mass m^* located at a distance z from the surface of a semi-infinite material that has the bottom of the conduction band above the vacuum level. The material is assumed to have its surface in the plane xy, occupying the upper half-space $z>0$ and being described by a dielectric response function $\epsilon(\omega)$, which depends only upon frequency as

$$\epsilon(\omega)=\epsilon_\infty+\frac{\epsilon_s-\epsilon_\infty}{1-\omega^2/\omega_T^2}\ , \tag{2.1}$$

where ϵ_s and ϵ_∞ are the static and optical dielectric constant of the crystal, respectively, and ω_T is the transverse optical-phonon frequency. By assuming that the electron couples only with the surface optical phonons, the Hamiltonian of the system may be written as

$$\begin{aligned}H=&\frac{1}{2m^*}f(z)P^2+\frac{1}{2m^*}p_z f(z)p_z+\mathscr{V}(z)\\&+\sum_{\vec{K}}\hbar\omega_s a^\dagger_{\vec{K}}a_{\vec{K}}\\&+\sum_{\vec{K}}(V^*_{\vec{K}}e^{-i\vec{K}\cdot\vec{R}}a^\dagger_{\vec{K}}+\text{H.c})e^{-K|z|}\ ,\end{aligned} \tag{2.2}$$

where $K=|\vec{K}|$ and

$$f(z)=\Theta(z)+(m^*/m)\Theta(-z)\ . \tag{2.3}$$

The electron position and momentum operators are $\vec{r}=(\vec{R},z)$ and $\vec{p}=(\vec{P},p_z)$, respectively. $a_{\vec{K}}$ and $a^\dagger_{\vec{K}}$ are the annihilation and creation operators of a surface excitation with wave number $\vec{K}$ parallel to the surface. The frequency of the surface mode is obtained by the well-known condition

$$\epsilon(\omega_s)=-1\ , \tag{2.4}$$

which gives

$$\omega_s^2=\frac{\epsilon_s+1}{\epsilon_\infty+1}\omega_T^2\ , \tag{2.5}$$

$\mathscr{V}(z)$ is the one-particle potential representing the Hartree field of ions and electrons acting on the electron when it is inside the crystal. Such a band-structure effect is described here by a simple potential step at the surface $z=0$ with step height $\mathscr{V}_0$; that is,

$$\mathscr{V}(z)=\mathscr{V}_0\Theta(z)\ . \tag{2.6}$$

The Fourier coefficient of the electron–surface-mode interaction $V_{\vec{K}}$, given by

$$V_{\vec{K}}=-2\pi i(\hbar e^2\delta/2A\omega_s)^{1/2}(1/\sqrt{K})\ , \tag{2.7}$$

where A is the surface area, is dependent on the parameter δ, which has different values for each type of surface excitation. For plasmons, for example, it is

$$\delta=\omega_s^2/2\pi\ , \tag{2.8}$$

and for phonons it is

$$\delta=\frac{\omega_s^2}{2\pi}\left[\frac{\epsilon_s-1}{\epsilon_s+1}-\frac{\epsilon_\infty-1}{\epsilon_\infty+1}\right]. \tag{2.9}$$

By analogy with the bulk-polaron problem we introduce the traditional dimensionless electron–surface-excitation coupling constant α_s as

$$\alpha_s=(2\pi e^2\delta/\omega_s^2)(m/2\hbar^3\omega_s)^{1/2}\ . \tag{2.10}$$

The Hamiltonian, Eq. (2.2), is invariant under translations, and the total momentum parallel to the surface, that is, the sum of electron momentum $\vec{\mathrm{P}}$ and surface optical-phonon momenta

$$\vec{\mathrm{P}}_t=\vec{\mathrm{P}}+\sum_{\vec{\mathrm{K}}}\hbar\vec{\mathrm{K}}a^\dagger_{\vec{\mathrm{K}}}a_{\vec{\mathrm{K}}} \tag{2.11}$$

is conserved, i.e., $[H,\vec{\mathrm{P}}_t]=0$. As stated above, the surface-polaron state $|\psi\rangle$ will be postulated to be a product of an electron wave function and a coherent phonon state. Consequently this surface-polaron state is not an eigenstate of the total momentum operator $\vec{\mathrm{P}}_t$ and therefore does not belong in any representation of translation group. For this reason the minimization of the energy should be performed by constraining the total momentum operator $\vec{\mathrm{P}}_t$. We will do the variation in the following way:

$$\delta\langle\psi|(H-\vec{\mu}\cdot\vec{\mathrm{P}}_t)|\psi\rangle=0\ , \tag{2.12}$$

where $\vec{\mu}$ is introduced as a Lagrange multiplier to keep the expected value of the total momentum a constant. It turns out to be identified as the velocity of the surface polaron.

The technique introduced by Huybrechts[22] is to employ a modified Lee-Low-Pines[10] canonical transformation S, defined as

$$S=\exp\left[-i\eta\sum_{\vec{\mathrm{K}}}\vec{\mathrm{K}}\cdot\vec{\mathrm{R}}a^\dagger_{\vec{\mathrm{K}}}a_{\vec{\mathrm{K}}}\right], \tag{2.13}$$

where η is a variational parameter to be determined upon minimizing the ground-state energy of the system. We now proceed in a similar fashion, by subjecting the Hamiltonian

$$\mathscr{H}=H-\vec{\mu}\cdot\vec{\mathrm{P}}_t \tag{2.14}$$

to the unitary transformation S. We find

$$\mathscr{H}'=S^{-1}\mathscr{H}S=\frac{1}{2m^*}p_z f(z)p_z+\mathscr{V}(z)+\frac{f(z)}{2m^*}\left[\vec{\mathrm{P}}-\eta\sum_{\vec{\mathrm{K}}}\hbar\vec{\mathrm{K}}a^\dagger_{\vec{\mathrm{K}}}a_{\vec{\mathrm{K}}}\right]^2+\sum_{\vec{\mathrm{K}}}(\hbar\omega_s-\hbar\vec{\mu}\cdot\vec{\mathrm{K}})a^\dagger_{\vec{\mathrm{K}}}a_{\vec{\mathrm{K}}}$$
$$-\vec{\mu}\cdot\left[\vec{\mathrm{P}}-\eta\sum_{\vec{\mathrm{K}}}\hbar\vec{\mathrm{K}}a^\dagger_{\vec{\mathrm{K}}}a_{\vec{\mathrm{K}}}\right]+\sum_{\vec{\mathrm{K}}}\{V^*_{\vec{\mathrm{K}}}\exp[-i(1-\eta)\vec{\mathrm{K}}\cdot\vec{\mathrm{R}}]a^\dagger_{\vec{\mathrm{K}}}+\text{H.c.}\}e^{-K|z|}\ . \tag{2.15}$$

It should be interesting to note that this expression recovers the Lee-Low-Pines weak-coupling interaction results for the two-dimensional system in the case when $\eta=1$. On the other hand, in limit $\eta\to0$ we obtain the strong-coupling approximation recently discussed by Hipólito.[15]

Under the second Lee-Low-Pines canonical transformation,

$$U=\exp\left[\sum_{\vec{\mathrm{K}}}(\xi_{\vec{\mathrm{K}}}a^\dagger_{\vec{\mathrm{K}}}-\xi^*_{\vec{\mathrm{K}}}a_{\vec{\mathrm{K}}})\right], \tag{2.16}$$

where $\xi_{\vec{\mathrm{K}}}$ is a variational function, the Hamiltonian $\mathscr{H}'$, Eq. (2.15), transforms as

$$\mathscr{H}''=U^{-1}\mathscr{H}'U=\frac{1}{2m^*}p_z f(z)p_z+\mathscr{V}(z)+\frac{f(z)}{2m^*}\left[\vec{\mathrm{P}}-\eta\sum_{\vec{\mathrm{K}}}\hbar\vec{\mathrm{K}}|\xi_{\vec{\mathrm{K}}}|^2\right]^2-\vec{\mu}\cdot\left[\vec{\mathrm{P}}-\eta\sum_{\vec{\mathrm{K}}}\hbar\vec{\mathrm{K}}|\xi_{\vec{\mathrm{K}}}|^2\right]$$
$$+\sum_{\vec{\mathrm{K}}}\left[\hbar\omega_s+\frac{\eta^2\hbar^2K^2}{2m^*}f(z)-\hbar\vec{\mu}\cdot\vec{\mathrm{K}}\right]|\xi_{\vec{\mathrm{K}}}|^2$$
$$+\sum_{\vec{\mathrm{K}}}\{V^*_{\vec{\mathrm{K}}}\exp[-i(1-\eta)\vec{\mathrm{K}}\cdot\vec{\mathrm{R}}]\xi^*_{\vec{\mathrm{K}}}+\text{H.c.}\}e^{-K|z|}+\mathscr{H}''_1\ , \tag{2.17}$$

where $\mathscr{H}''_1$ contains terms of no consequence for the calculation of the ground-state properties in which we are interested.

Following Huybrechts[22] we introduce the creation and annihilation operators $B_j^\dagger$ and B_j by

$$P_j=\left[\frac{m\hbar\lambda}{2}\right]^{1/2}(B_j^\dagger+B_j+P_{0j})\ , \tag{2.18a}$$

$$R_j = i\left[\frac{\hbar}{2m\lambda}\right]^{1/2}(B_j - B_j^\dagger)\ , \tag{2.18b}$$

where the index j stands for the electron coordinate parallel to the surface and λ and $\vec{P}_0$ are variational parameters. These expressions for P_j and R_j are then substituted into Eq. (2.17) to obtain a new representation for $\mathscr{H}''$, namely $\mathscr{H}'''$. Next we will evaluate the expectation value of this new Hamiltonian $\mathscr{H}'''$ for the ground-state wave function of the system, given as a product anzatz trial function by

$$|\psi\rangle = \phi(z)\,|0\rangle\ , \tag{2.19}$$

where $\phi(z)$ is a normalized function of electron coordinate only, as long as

$$\int_{-\infty}^{\infty} dz\,|\phi(z)|^2 = 1\ , \tag{2.20}$$

and $|0\rangle$ is the surface-phonon ground state, which is obtained from

$$a_{\vec{K}}\,|0\rangle = 0\ ,\quad B_j\,|0\rangle = 0\ ,\quad \langle 0|0\rangle = 1\ . \tag{2.21}$$

Taking into account the total momentum conservation, that is,

$$\left\langle \psi \left| U^{-1}S^{-1}\left[\vec{P} + \sum_{\vec{K}} \hbar\vec{K}\, a_{\vec{K}}^\dagger a_{\vec{K}}\right] SU \right| \psi \right\rangle = 0\ , \tag{2.22}$$

we obtain the expression for the expectation value,

$$F(\eta,\lambda,\xi_{\vec{K}},\vec{P}_0,\vec{\mu}) \equiv \langle\psi|\mathscr{H}'''|\psi\rangle\ , \tag{2.23}$$

which after some algebraic manipulation turns out to be

$$F(\eta,\lambda,\xi_{\vec{K}},\vec{P}_0,\vec{\mu}) = W\frac{\hbar\lambda}{2} + W\frac{\hbar\lambda}{4}P_0^2 + \left[\frac{m\hbar\lambda}{2}\right]^{1/2}\vec{\mu}\cdot\vec{P} + \sum_{\vec{K}}\left[\hbar\omega_s + W\eta^2\frac{\hbar^2K^2}{2m} - \hbar\vec{\mu}\cdot\vec{K}\right]|\xi_{\vec{K}}|^2$$
$$+ \sum_{\vec{K}}(V_{\vec{K}}^*\xi_{\vec{K}}^* + V_{\vec{K}}\xi_{\vec{K}})\exp\left[-\frac{(1-\eta)^2\hbar K^2}{4m\lambda}\right]M(\vec{K})$$
$$+ \int_{-\infty}^{\infty} dz\,\phi^*(z)\left[\frac{1}{2m^*}p_z f(z) p_z + \mathscr{V}(z)\right]\phi(z)\ , \tag{2.24}$$

where

$$W = (m/m^*)\int_{-\infty}^{\infty} dz\, f(z)\,|\phi(z)|^2 \tag{2.25}$$

and

$$M(\vec{K}) = \int_{-\infty}^{\infty} dz\,\phi^*(z)\exp(-K|z|)\phi(z)\ . \tag{2.26}$$

The variational function $\xi_{\vec{K}}$ and the parameter $\vec{P}_0$ are determined by performing the minimization of Eq. (2.24) with respect to both $\xi_{\vec{K}}$ and $\vec{P}_0$,

$$\frac{\delta F}{\delta \xi_{\vec{K}}} = 0\ ,\quad \frac{\delta F}{\delta \vec{P}_0} = 0\ . \tag{2.27}$$

We then find that

$$\xi_{\vec{K}} = -\frac{V_{\vec{K}}^* M(\vec{K})\exp[-(1-\eta)^2\hbar K^2/4m\lambda]}{\hbar\omega_s + W\eta^2\hbar^2K^2/2m - \hbar\vec{\mu}\cdot\vec{K}} \tag{2.28}$$

and

$$\vec{P}_0 = \left[\frac{2m}{\hbar\lambda}\right]^{1/2}\frac{\vec{\mu}}{W}\ . \tag{2.29}$$

By substituting these expressions for $\xi_{\vec{K}}$ and $\vec{P}_0$ back into F [Eq. (2.24)], and up to second order in the surface-polaron velocity $\vec{\mu}$, we find

$$F(\eta,\lambda,\vec{\mu}) = W\frac{\hbar\lambda}{2} - \sum_{\vec{K}}\frac{|V_{\vec{K}}|^2 M^2(\vec{K})\exp[-(1-\eta)^2\hbar K^2/2m\lambda]}{\hbar\omega_s + W\eta^2\hbar^2K^2/2m}$$
$$- \frac{m\mu^2}{2}\left[\frac{1}{W} + \frac{\hbar^2}{m}\sum_{\vec{K}}\frac{|V_{\vec{K}}|^2 M^2(\vec{K})K^2\exp[-(1-\eta)^2\hbar K^2/2m\lambda]}{(\hbar\omega_s + W\eta^2\hbar^2K^2/2m)^3}\right]$$
$$+ \int_{-\infty}^{\infty} dz\,\phi^*(z)\left[\frac{1}{2m^*}p_z f(z) p_z + \mathscr{V}(z)\right]\phi(z)\ . \tag{2.30}$$

We finally obtain the general expressions for the ground-state energy E_0, the surface-polaron effective mass m_{sp}, and the mean number of surface phonons N in the cloud around the electron:

$$E_0=W\frac{\hbar\lambda}{2}-\sum_{\vec{K}}\frac{|V_{\vec{K}}|^2M^2(\vec{K})\exp[-(1-\eta)^2\hbar K^2/2m\lambda]}{\hbar\omega_s+W\eta^2\hbar^2K^2/2m}+\int_{-\infty}^{\infty}dz\,\phi^*(z)[p_zf(z)p_z+\mathscr{V}(z)]\phi(z)\,, \tag{2.31}$$

$$\frac{m_{sp}}{m}=\frac{1}{W}+\frac{\hbar^2}{m}\sum_{\vec{K}}\frac{|V_{\vec{K}}|^2M^2(\vec{K})K^2\exp[-(1-\eta)^2\hbar K^2/2m\lambda]}{(\hbar\omega_s+W\eta^2\hbar^2K^2/2m)^3}\,, \tag{2.32}$$

$$N=\left\langle\psi\left|U^{-1}S^{-1}\sum_{\vec{K}}a^{\dagger}_{\vec{K}}a_{\vec{K}}SU\right|\psi\right\rangle=\sum_{\vec{K}}|\xi_{\vec{K}}|^2=\sum_{\vec{K}}\frac{|V_{\vec{K}}|^2M^2(\vec{K})\exp[-(1-\eta)^2\hbar K^2/2m\lambda]}{(\hbar\omega_s+W\eta^2\hbar^2K^2/2m)^2}\,. \tag{2.33}$$

It should be noted that in the weak-coupling limit, that is, $\eta=1$, Evans and Mills[3] presented a very illuminating discussion about the general features of these expressions. For large coupling constants, $\eta\to0$, a few remarks were presented by one of us.[15] We will explore here the results of this model calculation by assuming two distinct forms for the variational wave function of the electron in the next section.

III. APPLICATION OF THE MODEL

A. Electron localized in its z coordinate

As our first application of the present method we will study the ground state of an electron located in the z-coordinate system at a fixed distance $z=z_0$ from the surface of a material; as a consequence we take for the density $|\phi(z)|^2$ the δ function $\delta(z+z_0)$ with $z_0>0$. In this case it is a straightforward matter of calculation to find an expression for the ground-state energy. We obtain

$$E_0=\frac{\lambda}{2}-\alpha_s\int_0^{\infty}dx\frac{\exp[-(1-\eta)^2x^2/\lambda-2xz_0]}{1+\eta^2x^2}\,. \tag{3.1}$$

From here on we adopt units in which energy is taken in units of the optical-surface-phonon energy $\hbar\omega_s$, λ in units of the frequency ω_s, and lengths in units of the average distance of the electron from the surface, $z_s=(\hbar/2m\omega_s)^{1/2}$. The second term in Eq. (3.1), which is the shift in energy of the electron arising from the interaction with the surface modes, is in this case the so-called image potential. For large values of z_0 the interaction term, $V(z_0)$ reduces to the familiar classical image potential result, that is,

$$V(z_0)=-\frac{1}{\hbar\omega_s}\left[\frac{2m\omega_s}{\hbar}\right]^{1/2}\left[\frac{\epsilon_s-1}{\epsilon_s+1}-\frac{\epsilon_\infty-1}{\epsilon_\infty+1}\right]\frac{e^2}{4z_0}$$

$$=-\frac{\alpha_s}{2z_0}\,. \tag{3.2}$$

When the electron is close enough to the surface, say $z_0<1$, the classical image potential $V(z_0)$ is greatly modified. Therefore it does not diverge at $z_0=0$ as in the classical case. Thus, as $z_0\to0$, the interaction potential energy remains finite:

$$V(z_0\to0)=-\tfrac{1}{2}\pi\alpha_s$$

in the weak-coupling regime, and

$$V(z_0\to0)=-\tfrac{1}{4}\pi\alpha_s^2$$

in the strong-coupling regime. It is interesting to note that this rounding off of the divergence in the classical image potential was described earlier by Sak[4] and Evans and Mills[3] in the weak-coupling limit. Recently, Hipólito[15] presented the same results as ours in both weak- and strong-coupling regimes.

In general, the expression for the ground-state energy given by Eq. (3.1) must be minimized with respect to both variational parameters η and λ for each value of z_0 and the coupling constant α_s. Hence, with the optimum values of η and λ numerically determined from the equations

$$\frac{\delta E_0}{\delta\eta}=0\,,\quad\frac{\delta E_0}{\delta\lambda}=0\,, \tag{3.3}$$

we have obtained the ground-state energy of the surface polaron as a function of the coupling constant α_s for the cases $z_0=0$ and 0.1. As can be seen from Fig. 1, the energy has two distinct branches. The first branch is a straight line that corresponds to the weak-coupling limit and terminates at the point α_{sf}. The second branch is a curved line asymptotically

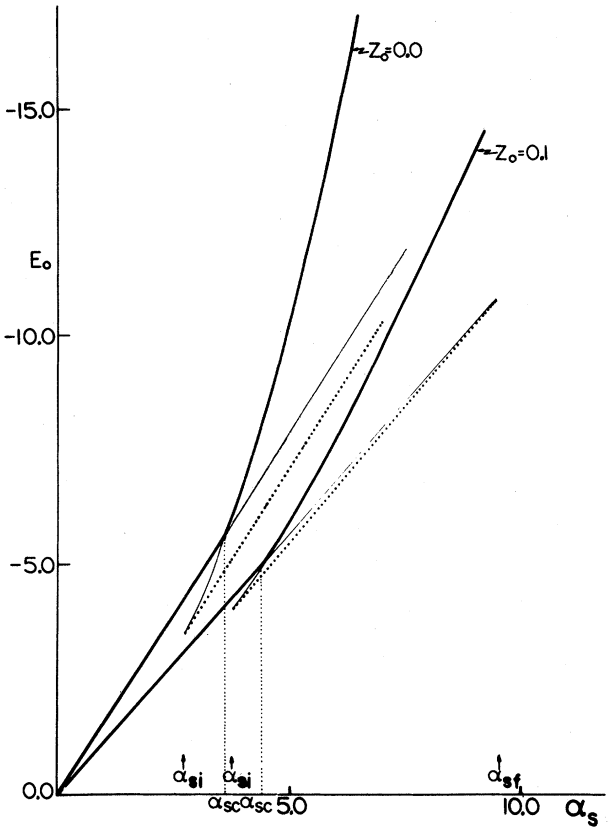

FIG. 1. Ground-state energy in units of $\hbar\omega_s$ of the surface polaron as function of the coupling constant α_s for two values of z_0, the distance of the electron from the surface. The thick solid part of each curve corresponds to a stable solution with lower energy. The thin solid line corresponds to the second-lowest solution representing a metastable state which is the self-trapping state or the nearly-free state according to whether $\alpha_s < \alpha_{sc}$ or $\alpha_s > \alpha_{sc}$. The dotted line corresponds to the maximum representing the unstable solution.

expressed in a quadratic form that begins at the point α_{si} and corresponds to the strong-coupling regime. The crossing point α_{sc} of the two branches gives the first-order phase-transition point. At this critical point the surface-polaron state changes from a nearly-free-type state to a self-trapped one. There is also a third energy branch corresponding to the maximum, which is related to the unstable solution of Eq. (3.3).

In Fig. 2 we plot the best value of the parameter η that minimizes the ground-state energy as a function of the coupling constant. As can be seen, an abrupt change in η occurs at the critical point $\alpha_s = \alpha_{sc}$. For each curve, the thick solid line corresponds to the stable solution with lower energy, the dotted line corresponds to the maximum energy, and the thin solid line corresponds to a metastable solution.

With η and λ being the best parameters for minimizing the energy, we are able to compute the effective mass of the surface polaron as well as the mean number of surface phonons around the electron. Thus Eqs. (2.32) and (2.33) reduce in this case to

$$\frac{m_{sp}}{m} = 1 + 2\alpha_s \int_0^\infty dx \frac{\exp[-(1-\eta)^2 x^2/\lambda - 2xz_0]}{(1+\eta^2 x^2)^3} \tag{3.4}$$

and

$$N = \alpha_s \int_0^\infty dx \frac{\exp[-(1-\eta)^2 x^2/\lambda - 2xz_0]}{(1+\eta^2 x^2)^2} . \tag{3.5}$$

The numerical calculation of Eqs. (3.4) and (3.5) was performed, and the results as a function of the coupling constant for the cases $z_0 = 0$ and 0.1 are displayed in Figs. 3 and 4. The first-order phase-transition behavior is most clearly seen by a discontinuous change of the mass and the mean number of surface phonons at the critical coupling constant α_{sc}.

Let us now discuss the characteristic behaviors of the surface-polaron ground-state energy, the effective mass, and the mean number of surface phonons around the electron in both limits of weak and strong coupling for the case where the electron motion is restricted to the surface, that is, $z_0 = 0$. As stated before, in the weak-coupling theory we have small α_s and $\eta = 1$. Then in this limit it is clear from Eq. (3.1) that a minimum of E_0 occurs at $\lambda = 0$. In this case a straightforward calculation leads to the following expression for the ground-state energy (which actually is the interaction potential energy):

$$E_0 = -\tfrac{1}{2}\pi\alpha_s . \tag{3.6}$$

For the effective mass we obtain

$$\frac{m_{sp}}{m} = 1 + \tfrac{1}{8}\pi\alpha_s , \tag{3.7}$$

and for the mean number of surface phonons

$$N = \tfrac{1}{4}\pi\alpha_s \tag{3.8}$$

In the strong-coupling regime, which corresponds to large values of α_s, we have $\eta = 0$, resulting then for the energy E_0,

$$E_0 = -\tfrac{1}{8}\pi\alpha_s^2 . \tag{3.9}$$

The best-fit value of the variational parameter λ was found to be $\lambda = \frac{1}{4}\pi\alpha_s^2$. In this strong-coupling limit

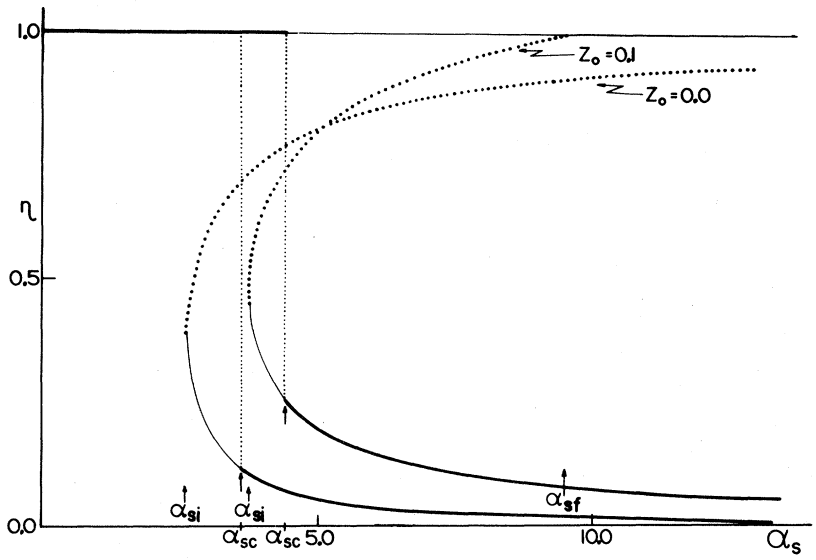

FIG. 2. Variational parameter η, which minimizes the ground-state energy as function of the surface-polaron coupling constant α_s for two values of z_0, the distance of the electron from the surface. The curves are described in the same way as in Fig. 1.

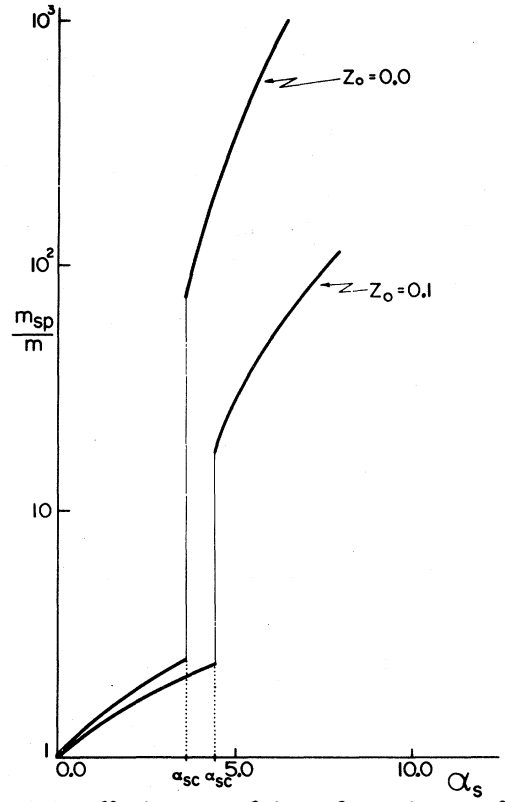

FIG. 3. Effective mass of the surface polaron as function of the coupling constant α_s for two values of z_0, the distance of the electron from the surface.

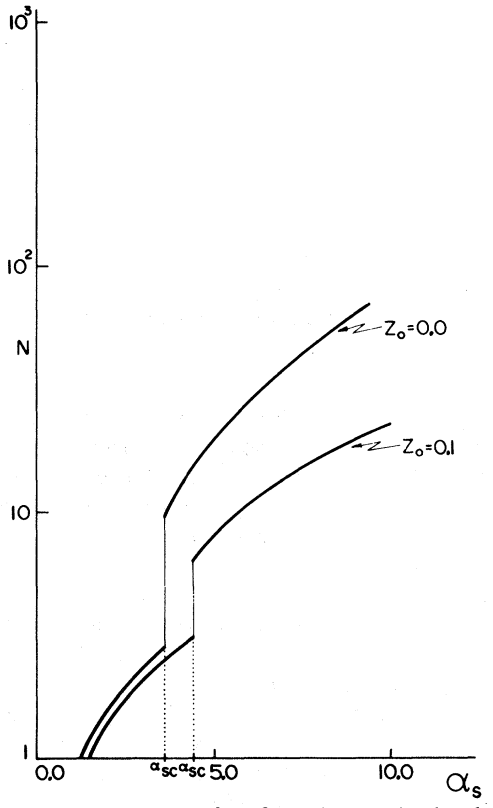

FIG. 4. Mean number of surface phonons in the cloud around the electron as function of the coupling constant α_s for two values of z_0, the electron distance from the surface.

we obtain for the effective mass

$$\frac{m_{\rm sp}}{m}=1+\tfrac{1}{16}\pi^2\alpha_s^4 , \tag{3.10}$$

and for the mass number of surface phonons

$$N=\tfrac{1}{4}\pi\alpha_s^2 . \tag{3.11}$$

The results are in both regimes of weak- and strong-coupling constants the same as those obtained earlier from different approaches.[1,3,4,15]

Finally, it should be interesting to note that in the two limiting cases the principal contribution to the ground-state energy of the surface polaron came from the self-induced potential. At small coupling-constant values the surface polaron is quasifree and becomes trapped by the self-induced potential as the coupling constant exceeds the critical value α_{sc}.

B. Variational wave function

The first variational calculation allowing the electron wave to penetrate the crystal but restricting it to the weak or intermediate-coupling constant regime is that of Evans and Mills.[3] Here, we will follow their calculation by choosing a two-parameter trial wave function $\phi(z)$, which has the form

$$\phi(z)=\begin{cases} Ae^{-\gamma z}, & z>0 \\ B(z+z')e^{\beta z}, & z<0 . \end{cases} \tag{3.12}$$

In the case where $\mathscr{V}_0$ is large compared to the surface-polaron ground-state energy, the parameter γ, which measures the depth of penetration of the wave function into the medium, may be taken as a fixed parameter and given by $\gamma=(2m^*\mathscr{V}_0/\hbar)^{1/2}$. In general, γ must be treated as a variational parameter.

By imposing the requirement that $\phi(z)$ be continuous at the surface with slopes in the vacuum and in the material fitted at the surface and the normalization condition, we find for the values of the parameters A, B, and z'

$$\begin{aligned} A&=\left[\frac{4\gamma\beta^3}{\gamma+2\beta}\right]^{1/2}\frac{1}{\gamma+\beta} , \\ B&=-\left[\frac{4\gamma\beta^3}{\gamma+2\beta}\right]^{1/2} , \\ z'&=\frac{1}{\gamma+\beta} . \end{aligned} \tag{3.13}$$

In the calculation we perform below, with the parameter γ controlled by $\mathscr{V}_0$, the wave function of the electron perpendicular to the surface turns out to have only a simple remaining variational parameter β. In this model, the surface-polaron ground-state energy [Eq. (2.31)], the effective mass [Eq. (2.32)], and the mean number of the surface phonons around the electron [Eq. (2.33)], may easily be rewritten as

$$E_0=\frac{\gamma\beta^2}{\gamma+2\beta}\left[1+2\gamma\beta\left[1-\frac{m}{m^*}\right]\frac{1}{(\gamma+\beta)^2}\right] +W\frac{\lambda}{2}-\alpha_s\int_0^\infty dx\frac{M^2(x)\exp[-(1-\eta)^2x^2/\lambda]}{1+W\eta^2x^2} , \tag{3.14}$$

$$\frac{m_{\rm sp}}{m}=\frac{1}{W}+2\alpha_s\int_0^\infty dx\frac{x^2M^2(x)\exp[-(1-\eta)^2x^2/\lambda]}{(1+W\eta^2x^2)^3} \tag{3.15}$$

and

$$N=\alpha_s\int_0^\infty dx\frac{M^2(x)\exp[-(1-\eta)^2x^2/\lambda]}{(1+W\eta^2x^2)^2} , \tag{3.16}$$

where

$$W=1-2\beta^3\left[1-\frac{m}{m^*}\right]\frac{1}{(\gamma+2\beta)(\gamma+\beta)^2} \tag{3.17}$$

and

$$M(x)=\frac{\gamma}{\gamma+2\beta}\left[\frac{2\beta}{x+2\beta}\right]^3 \times\left[1+\frac{x+2\beta}{\gamma+\beta}+\frac{(x+2\beta)^2(x+\gamma+\beta)}{(x+2\gamma)(\gamma+\beta)^2}\right] . \tag{3.18}$$

As before, the energy is expressed in units of $\hbar\omega_s$, λ in units of ω_s, and the lengths in units of $z_s=(\hbar/2m\omega_s)^{1/2}$, the average distance of the electron from the surface. The parameters η, λ, and β must be determined by minimizing Eq. (3.14) through the extremum point conditions:

$$\frac{\delta E_0}{\delta\eta}=\frac{\delta E_0}{\delta\lambda}=\frac{\delta E_0}{\delta\beta}=0 . \tag{3.19}$$

We have carried out all the calculations with the assumption that $m=m^*$.

In Fig. 5 we plot the surface-polaron ground-state energy as a function of the coupling constant α_s for the cases $\gamma=10$ and ∞ (no penetration of the electron wave function into the crystal). As can be seen, we found an energy that has two distinct branches. The first branch corresponds to the weak-coupling approximation appropriate for a small coupling con-

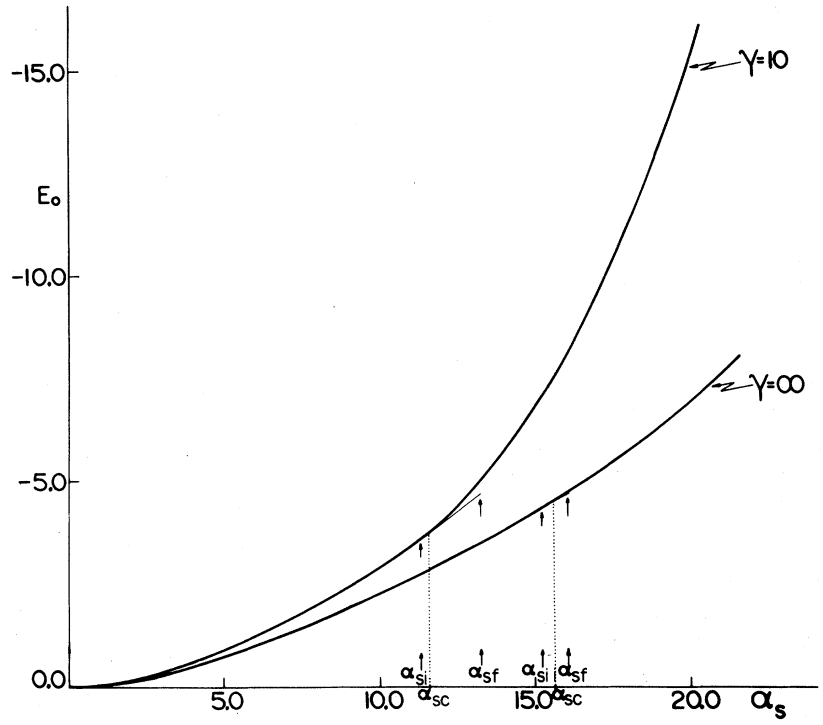

FIG. 5. Ground-state energy as function of the surface-polaron coupling constant α_s for two values of γ, the inverse of the depth of penetration of the wave function into the material. The notations $\alpha_{si},\alpha_{sc},\alpha_{sf}$ as well as the curves are described in the text.

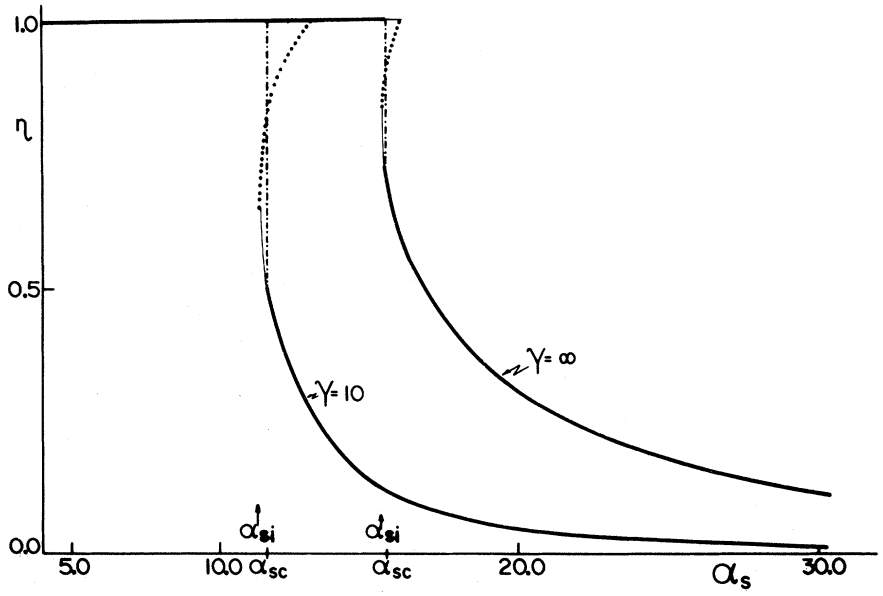

FIG. 6. Variational parameter η, which minimizes the ground-state energy as function of the surface-polaron coupling constant α_s for two values of γ, the inverse of the depth of penetration of the electron wave function into the material. The curves are described in the same way as in Fig. 1.

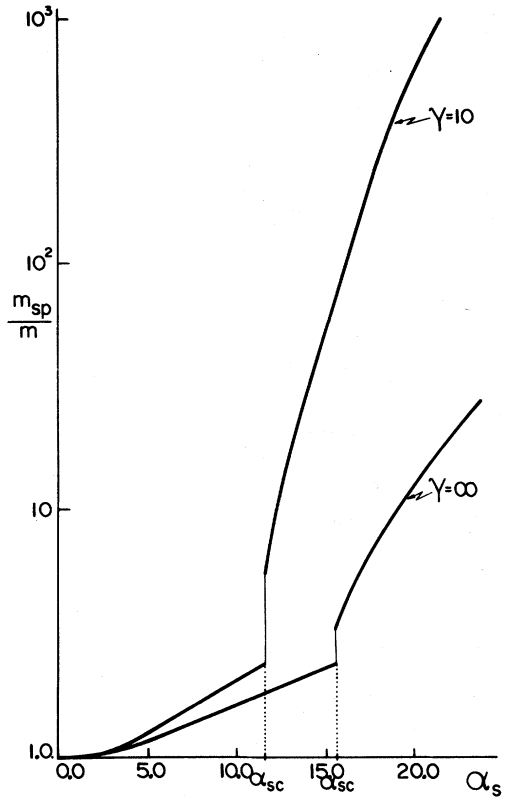

FIG. 7. Effective mass of the surface polaron as function of the coupling constant α_s for two values of γ, the inverse of the depth of the penetration of the electron wave function into the material.

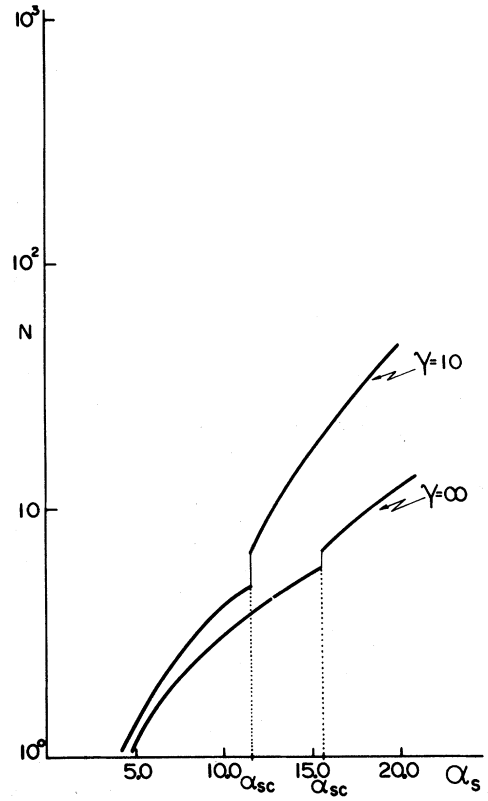

FIG. 8. Mean number of the surface phonons in the cloud around the electron as function of the coupling constant α_s for two values of γ, the inverse of the depth of the penetration of the electron wave function into the material.

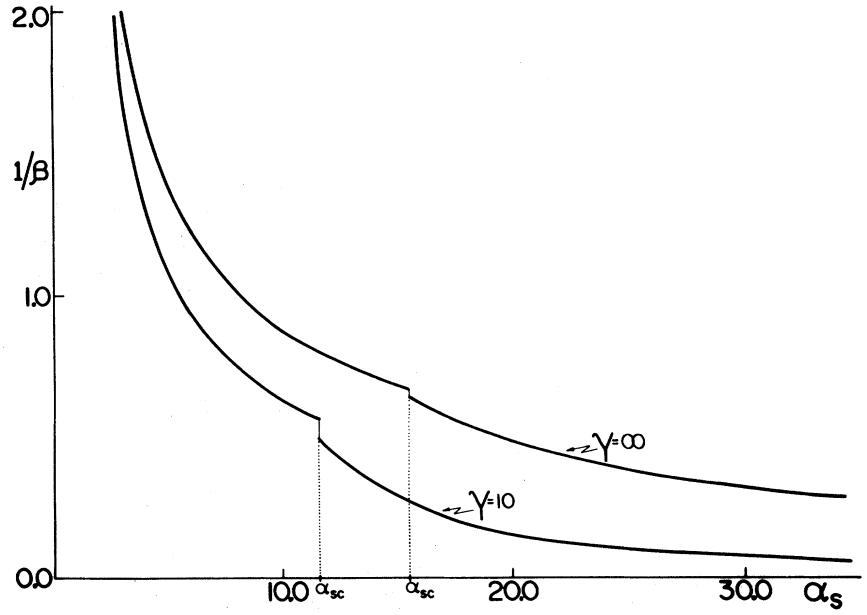

FIG. 9. Spatial localization of the electron perpendicular to the surface as function of the coupling constant α_s for two values of γ, the inverse of the depth of the electron wave function into the material.

stant α_s and presented by Evans and Mills[3] within the Lee-Low-Pines theory. This branch crosses the second one at a critical point $\alpha_s = \alpha_{sc}$ and terminates at α_{sf}. The second branch beginning at the point α_{si} corresponds to the strong-coupling approximation as discussed in an earlier paper by Hipólito.[15] The surface polaron undergoes a first-order phase transition from a nearly-free-type state to a self-trapping one at the crossing point of these branches. This transition is accompanied by a discontinuous change of the parameter η as shown in Fig. 6, where the values of η that minimize the ground-state energy are plotted as a function of the surface-polaron coupling constant α_s. The solid lines correspond to the minima of the ground-state energy, while the dotted line corresponds to the maximum. As the parameter γ decreases, that is, when the electron wave penetrates more deeply into the material and consequently the wave function becomes more compacted to the surface, the value of the transition point α_{sc} shifts to a small one. In such a way the electron can be trapped most easily by the surface modes.

The first-order phase-transition behavior from a quasifree surface-polaron state to a self-trapped one is even more dramatically seen in the effective mass, the mean number of surface phonons around the electron, and the spatial localization of the electron perpendicular to the surface, as is shown in Figs. 7–9. A very rapid change in these physical quantities occurs as the coupling constant exceeds the critical value α_{sc}.

IV. CONCLUSIONS

In this paper we have applied a simple unitary-transformation method to investigate the ground-state properties of a surface polaron. We have considered the case where the electron lies outside the crystal and, as a consequence, interacts with the surface phonons only. The numerical results have shown the occurrence of an abrupt change in the ground-state energy, the effective mass, the mean number of surface phonons in the cloud around the electron, and the spatial localization of the electron perpendicular to the surface at a certain critical value of the coupling constant. In such a first-order phase-transition behavior the surface polaron changes at this critical value of α_s from a nearly-free-state type to a self-trapped state. We feel that the results presented here give a good picture of some qualitative aspects of an electron self-trapped by the surface modes. We also hope that our theoretical predictions can be experimentally confirmed in the near future.

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[1]G. A. Farias, N. Studart, and O. Hipólito, Solid State Commun. 43, 95 (1982).
[2]N. Tokuda (unpublished).
[3]E. Evans and D. L. Mills, Solid State Commun. 11, 1093 (1972); Phys. Rev. B 8, 4004 (1973).
[4]J. Sak, Phys. Rev. B 6, 3981 (1972).
[5]G. Barton, J. Phys. C 14, 3975 (1981).
[6]G. Barton and M. Babiker, J. Phys. C 14, 4951 (1981).
[7]R. M. Nieminen and C. H. Hodges, Phys. Rev. B 18, 2568 (1978).
[8]N. Barberan and P. M. Echenique, Phys. Rev. B 19, 5431 (1979).
[9]M. Rona and A. Erçelebi, *Physics of Semiconductors* (IOP, London, 1979).
[10]T. D. Lee, F. Low, and D. Pines, Phys. Rev. 90, 297 (1953).
[11]S. I. Pekar, *Untersuchungen über die Elektronemtheorie der Kristalle* (Akademic, Berlin, 1954).
[12]T. D. Clark, Solid State Commun. 16, 861 (1975).
[13]D. M. Larsen, Phys. Rev. 144, 697 (1966).
[14]W. J. Huybrechts, Solid State Commun. 28, 95 (1978).
[15]O. Hipólito, Solid State Commun. 32, 515 (1979); J. Phys. C 12, 4667 (1979).
[16]J. M. Luttinger and C. Y. Lu, Phys. Rev. B 21, 4251 (1980).
[17]Y. Toyozawa, Pro. Theor. Phys. 26, 29 (1961).
[18]A. Sumi and Y. Toyozawa, J. Phys. Soc. Jpn. 35, 137 (1973).
[19]R. Manka, Phys. Lett. 67A, 311 (1978); Phys. Status Solidi B 93, 53 (1979).
[20]R. Manka and M. Suffczyński, J. Phys. C 13, 6369 (1980).
[21]H. Shoji and N. Tokuda, J. Phys. C 14, 1231 (1981).
[22]W. J. Huybrechts, J. Phys. C 9, L211 (1976); 10, 3761 (1977).