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The phase diagram of the tight-binding Fröhlich polaron

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Abstract. We consider the ground-state energy of a tight-binding polaron in a polar crystal. This system is represented by the Fröhlich Hamiltonian in which the effective-mass kinetic term is replaced by the kinetic energy of an electron in the lattice potential. Also, a Debye cut-off is made on the phonon wavevectors. We write this Hamiltonian in a tight-binding representation and evaluate an upper bound to its ground-state energy using the Fock approximation of Matz and Burkey. This treatment is valid for any coupling strength and any degree of adiabaticity. We find three possible configurations: a weak-coupling band state, a strong-coupling band state and a self-trapped state. The existence of these states depends on the value of two parameters: the electron–phonon coupling strength and the electronic bandwidth. We also evaluate the limits of validity of the continuum approximation for crystals of finite bandwidth by evaluating explicitly the corrections to the continuum approximation. We conclude that for small electron–phonon coupling ($\alpha < 2.7$) the continuum approximation is very good, that the strong-coupling band state does not exist in real crystals and that the self-trapped state can be found in narrow-band polar materials.

1. Introduction

In a wide-band polar semiconductor or insulator, the Fröhlich polaron is usually described in the continuum approximation [1]. The whole band structure is approximated by a unique parabolic conduction band populated with a single electron. The electron–lattice interactions are dominated by the electron–longitudinal-optical (LO) phonon interactions. Also the Brillouin zone is considered as unbounded (no Debye cut-off is applied on the phonon wavevectors). This description is valid for a wide conduction band, in which case the electron is limited to the bottom of the band and the polaron radius is much larger than the lattice parameter. For a narrow band, the electron can probe the whole band and a parabolic kinetic energy is clearly a bad approximation. Furthermore, the phonon wavevectors need to be limited to the first Brillouin zone to take into account the discreteness of the lattice.

In a narrow-band material, the bandwidth can be so small that the polaron becomes self-trapped [2]. The polaron then does not have any kinetic energy. It only has a potential energy related to the induced deformation of the lattice. It is called a small polaron. This state cannot be obtained in the framework of the continuum approximation. A Debye cut-off is essential to describe this state; otherwise, the polaron would become infinitely localized because of the absence of a positive kinetic term to counterbalance the trapping energy. The discreteness of the lattice is essential to get a finite result: it forbids the electron to localize on a scale smaller than the lattice parameter.

To describe situations where neither of these asymptotic descriptions is valid and to describe the transition between these two states, several approaches have been used. One

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of these consists in calculating corrections to the continuum approximation used in the Fröhlich Hamiltonian. This has been done by Lépine and Frongillo [3], using a Debye cut-off and the $k \cdot q$ representation of Zak [4] and by Paranjape and Panat [5] using a discrete lattice model for the polaron. Another approach consists in using a polaron Hamiltonian on which the effective-mass approximation has not been effected. This Hamiltonian is often called that of a tight-binding polaron for non-polar electron–phonon interactions. It has been extensively studied in the context of small-polaron theories by Holstein [6], Emin [7] and Klamt [8] with variational approaches and by de Raedt and Lagendijk [9] who used a Monte Carlo approach. In the case of polar interactions, it was first treated by Tiablikov and by Yamashita and Kurosawa in the adiabatic limit [10]. Later, Lépine and Frongillo treated this Hamiltonian in the non-adiabatic limit [11]. They find a self-trapped state for a narrow-band material with strong electron–phonon interaction and a band state in the opposite limit.

In the present paper, we calculate the ground-state energy of the tight-binding polar polaron. The whole problem is treated in a tight-binding basis and a Debye cut-off is applied on the phonon wavevectors. An upper bound to this energy is found, using the Fock approximation of Matz and Burkey that is known to be valid for any coupling strengths in the continuum case (for a wide band) [12]. This treatment is easily applied to the tight-binding Hamiltonian, when expressed in the appropriate basis. It leads to the three expected types of polaron state: the weak-coupling band state, the strong-coupling band state and the self-trapped state. Furthermore, the approach is valid in both the adiabatic and the non-adiabatic limits.

The paper is organized as follows. First, in the next section, we introduce the polaron Hamiltonian. We write it in a tight-binding basis. The variational ground-state energy is then obtained from the Fock approximation. In section 3, we derive asymptotic limits to this energy. These limits lead us to consider the three polaron states described above and to derive the values of the parameters for which each of these states has the lowest energy. We also give the corrections to the continuum approximation when one considers a conduction band of finite bandwidth. In section 4, we present our numerical results as phase diagrams. We also present the dependence of the polaron energy on the bandwidth to evaluate the size of the corrections to the continuum approximation. Finally, we conclude the paper by summarizing our results and by commenting on the applicability of the continuum approximation and on the possibility of observing the three phases in real crystals.

2. The Hamiltonian and its ground-state energy

We consider an electron in a polar crystal interacting with a periodic lattice potential $W(r)$ and with the longitudinal optical (LO) phonon field. The corresponding Hamiltonian was initially proposed by Tiablikov [10] and discussed later by Lépine and Frongillo [3, 11] to describe a free electron in a narrow-band polar crystal. The work of Tiablikov was done in the adiabatic limit while the latter authors worked in the non-adiabatic limit. In this section, we present an approach valid for both limits. As it will be shown, this Hamiltonian is general enough to exhibit the following configurations for the polaron: for large bandwidth, we find a weak-coupling band (WCB) polaron and a strong-coupling band (SCB) polaron while, for small bandwidth, we find a self-trapped (ST) polaron.

This Hamiltonian has three parts: an electronic part that describes the motion of the electron in a periodic potential (H_e), a free phonon part (H_ϕ) and an electron–phonon polar

interaction part that has the Fröhlich form (H_i) [13]. It is written:

$$H = H_e + H_\phi + H_i \tag{1}$$

where

$$H_e \equiv -\nabla_r^2 + W(r) \tag{2}$$

$$H_\phi \equiv \sum_l \left(b_l^\dagger b_l + \frac{1}{2} \right) \tag{3}$$

$$H_i \equiv \sum_l \left[V_l \, e^{il\cdot r} b_l + V_l^* e^{-il\cdot r} b_l^\dagger \right]. \tag{4}$$

This Hamiltonian is written in a trivial adaptation of the usual dimensionless system of units: $2m_e = \hbar = \hbar\omega = 1$. In this system, we have

$$V_l = -\frac{i}{l} \left(\frac{4\pi\alpha_e}{\Omega} \right)^{1/2} \qquad \alpha_e = \frac{e^2}{2\hbar\omega\tau_0} \left(\varepsilon_\infty^{-1} - \varepsilon_0^{-1} \right)$$

and

$$\tau_0 = \left(\frac{\hbar}{2m_e\omega} \right)^{1/2}.$$

In these equations, r and m_e are, respectively, the position and the *bare* mass of the electron and ω is the long-wavelength longitudinal optical (LO) phonon frequency. $b_l^\dagger$ and b_l are the second quantization operators for phonons of wavevector l. α_e represents the electron–phonon coupling constant (defined in the present case with the bare electron mass), V_l is the electron–phonon matrix element of the interaction potential and τ_0 is the polaron quantum radius, the natural unit of length in the problem. ε_0 and ε_∞ are the static and the high-frequency dielectric constants, respectively, and Ω is the system volume. The sums over l are restricted to the first Brillouin zone because the phonons cannot have wavelengths smaller than the lattice parameter. The Brillouin zone is thus approximated by a Debye sphere and the phonon wavevectors have to be smaller than L_e which is the Debye cut-off divided by τ_0 [3, 11].

We first write this Hamiltonian in a one-band tight-binding representation, using tight-binding wave-functions as a basis:

$$\phi_k(r) = |k\rangle = \frac{1}{\sqrt{N}} \sum_R e^{ik\cdot R} \phi(r - R) \tag{5}$$

where $\phi(r)$ is the atomic wave-function of the level corresponding to the band under consideration. This representation can be considered as an approximation of a Bloch representation for which the Wannier wave-functions have been replaced by atomic wave-functions. Within this tight-binding basis, the Hamiltonian becomes

$$H = \sum_k \epsilon_k C_k^\dagger C_k + \sum_l b_l^\dagger b_l + \sum_l \left[V_l \, b_l \rho_l \sum_k C_{k+l}^\dagger C_k + V_l^* b_l^\dagger \rho_{-l} \sum_k C_{k-l}^\dagger C_k \right] \tag{6}$$

where the $C_k^\dagger$ and C_k create or annihilate an electron in a tight-binding state k and J is the tight-binding transfer integral. H has been obtained in a tight-binding spirit: the matrix elements $\langle k|H_e|k'\rangle$ have been evaluated keeping only the first-neighbour contributions. The intrasite contributions being constants have been discarded and all other contributions are neglected. Also the matrix elements of the interaction terms ($\langle k|\exp(il\cdot r)|k'\rangle$) have been

evaluated keeping only the intrasite terms that give the most important contribution [11]. Finally the constant term in H_ϕ has been discarded. Also,

$$\rho_l = \int d^3r\ e^{il\cdot r}|\phi(r)|^2$$

is the Fourier transform of the atomic charge density and ϵ_k is the tight-binding energy of an electron in a rigid band and is given by

$$\epsilon_k = -J\sum_h e^{ik\cdot h} \tag{7}$$

h being the position vector of the nearest neighbours. It is important to note that in a plane-wave basis, without $W(r)$, the above Hamiltonian would reduce to the usual Fröhlich Hamiltonian [13]. This is also the case for a low-energy electron in a wide band ($J \gg \hbar\omega$) when the band structure can be approximated by a single parabolic band.

The ground-state energy of the polaron is now calculated, using the Fock approximation of Matz and Burkey [12] that is valid for any electron–phonon coupling strength. This treatment is easy to use and gives an upper bound to the ground-state energy of the polaron. It is also known, for the Fröhlich case, to be equivalent to the Feynman approach in the rigid-oscillator approximation (the one-particle model) [14]. It gives the well known results in the small- and large-coupling limits but also gives upper bounds for intermediate values. It is thus valid for any coupling and it will be also shown in the following to be valid in the adiabatic limit as well as in the non-adiabatic case (for wide or narrow bands). This approximation can easily be applied to the present tight-binding Hamiltonian and the following ground-state energy is obtained [12]:

$$E_0 = \int d^3r\ \Psi_0^*(r)\hat{\epsilon}_k(r)\Psi_0(r) + \sum_{l,n}\int d^3r\,d^3r'\,|V_l|^2|\rho_l|^2 e^{il\cdot(r-r')}\frac{\Psi_n(r)\Psi_n^*(r')}{E_0-1-E_n}\Psi_0(r')\Psi_0^*(r). \tag{8}$$

In this equation, $\hat{\epsilon}_k(r)$ is obtained from ϵ_k, replacing k by $-i\nabla_r$. $\{\Psi_n(r)\}$ forms a complete variational model spectrum, the E_n being its eigenvalues. The ground-state energy of this spectrum has to be the best approximation possible for the polaron wave-function.

We now have to choose a model spectrum. In the Fröhlich case, one usually chooses a Gaussian spectrum [3, 12, 14]. The model then consists in a free electron in interaction with a harmonic potential. In the present case, we chose to write the Hamiltonian in a tight-binding basis. The logical choice for the model is thus that of a tight-binding electron bound to a harmonic potential. It corresponds to the eigenvalues and eigenfunctions of the following Hamiltonian:

$$H_M = \hat{\epsilon}_k(r) + \beta'^4 r^2 \tag{9}$$

β' being a variational parameter to be determined by minimization. As written, it is not possible to solve this Hamiltonian analytically. We thus resort to an expansion of ϵ_k for small values of k. The new model Hamiltonian is thus defined by

$$H'_M = -6J - \frac{\nabla_r^2}{m_b} + \beta'^4 r^2 \tag{10}$$

where a cubic symmetry has been assumed for the nearest neighbours. Also, we have used the following definition of a tight-binding effective mass that is valid for any of the three cubic lattices:

$$m_b = 1/Jh^2 \tag{11}$$

h being the nearest-neighbour distance. This new model is expected to be at its best for large bands, in which case the electron is near the bottom of the band. It is also good for a narrow band: the electron is then no longer in a band state and the details of the band structure and of the model are not very important. The eigenvalues and eigenfunctions of this Hamiltonian are used as a model in the following.

The ground-state energy of the polaron is now obtained by substituting the above model spectrum into equation (8). The exact nature of the atomic wave-functions is not important here since we are not attempting a detailed band-structure calculation. It is however important that these functions decay over a distance of the order of an atomic distance. In the present case, for practical reasons, we model $\phi(r)$ with a Gaussian wave-function:

$$\phi(r) = \sqrt{\frac{\mu'^3}{\pi^{3/2}}} \exp\left(-\frac{\mu'^2 r^2}{2}\right) \tag{12}$$

where μ'^{-1} is chosen to be of the order of the extension of an atomic wave-function. Substituting equations (10) and (12) in equation (8) and defining β as $\beta = \beta'/\sqrt{m_b}$, μ as $\mu = \mu'/\sqrt{m_b}$, L as $L_e/\sqrt{m_b}$ and $\alpha = \alpha_e\sqrt{m_b}$, we obtain

$$E_0 = -6Je^{-\beta^2/4J} - \sqrt{\frac{2}{\pi}}\alpha\beta \int_0^\infty e^{-t} \frac{\operatorname{erf}\left[(L/\beta\sqrt{2})\left(1 - e^{-2\beta^2 t} + \beta^2/2\mu^2\right)^{1/2}\right]}{\left(1 - e^{-2\beta^2 t} + \beta^2/2\mu^2\right)^{1/2}} dt \tag{13}$$

where $\operatorname{erf}(x)$ is the error function. This energy has to be minimized with respect to β. In equation (13), all the lengths are given in units of $\tau_b = \tau_0/\sqrt{m_b}$ and all the wavevectors are given in units of τ_b^{-1}: it is thus written in terms of the effective band mass instead of the bare electronic mass. This is the same system of units as that used in the Fröhlich Hamiltonian [13]. We now look at the asymptotic limits of equation (13) to analyse the ground state of the polaron.

3. Asymptotic results

In this section, we analyse asymptotic limits of equation (13). To get useful results, we give the explicit relation existing between the following parameters: μ, J and L. First, we write the Debye cut-off as [11]

$$L_e = \left(\frac{3}{4\pi}\right)^{1/3} \frac{2\pi}{h}. \tag{14}$$

This Debye cut-off has been chosen such that the volume of the Debye sphere is equal to that of a simple cubic Brillouin zone ($(2\pi/h)^3$). For another lattice, the proportionality constant would differ but this relation would have the same form. Using this equation with equation (11), we get

$$L = \frac{L_e}{\sqrt{m_b}} = 2\pi\left(\frac{3}{4\pi}\right)^{1/3}\sqrt{J} = G\sqrt{J}. \tag{15}$$

We can thus use this relation to write our results as a function of J or, alternatively, of L. Also, the parameter μ scales with L, both being inversely proportional to the lattice parameter. In the following, we thus write

$$\mu = CL. \tag{16}$$

For a narrow band, C is large (the atomic wave-functions are localized). For a wide band, it can be slightly smaller than unity. Note that in the continuum limit, $h \to 0$ and that L and μ become infinitely large.

We first treat the continuum limit. An expansion for large values of J, L and μ gives

$$E_0 = -6J + \frac{3}{2}\beta^2 - \sqrt{\frac{2}{\pi}}\alpha\beta \int_0^\infty \frac{e^{-t}}{\sqrt{1-e^{-2\beta^2 t}}}\,dt. \tag{17}$$

Except for a constant term $(-6J)$ that corresponds to the bottom of the conduction band in the tight-binding approximation, this is exactly the expression for the ground-state energy found by Matz and Burkey [12] using the above formalism on the Fröhlich Hamiltonian or by Feynman in the rigid-oscillator approximation [14]. The corresponding weak- and strong-coupling asymptotic energies are the same as the first-order terms of a wide-band expansion of equation (13) and are given in the following.

We now consider the weak electron–phonon limit (the weak-coupling band case (WCB)). The electron wave-function is delocalized and β is known to minimize to zero (this can be shown by doing a small-β expansion of equation (13) and by minimizing with respect to β) [3, 12]. The ground-state energy of the polaron is then given by

$$E_0 = -6J - \frac{\alpha}{\sqrt{\pi}} \int_0^\infty e^{-t} \frac{\operatorname{erf}\left[L\left(t+1/4\mu^2\right)^{1/2}\right]}{\left(t+1/4\mu^2\right)^{1/2}}\,dt. \tag{18}$$

For a wide band, L (or $\sqrt{J}$) is large and we get

$$E_0 = -6J - \alpha + \frac{\alpha}{\sqrt{\pi}\mu}. \tag{19}$$

The first two terms are the usual weak-coupling results of the continuum Fröhlich polaron while the last term is a correction to the effective-mass approximation. For a narrow band, L is small and we find

$$E_0 = -6J - \frac{2}{\pi}\alpha L + \frac{2\alpha L^3}{3\pi}\left(1 + \frac{1}{4\mu^2}\right). \tag{20}$$

In this expression, the last term (in μ^{-2}) comes from the use of tight-binding wave-functions instead of plane waves to calculate the electron–phonon matrix element. The first term is the bottom of the conduction band while the other two give the self-energy of the polaron in this narrow-band case. This self-energy is that of a self-trapped polaron from which a small correction term in L^3 is subtracted to account for the delocalization energy related to the band.

In the strong-coupling limit, for a wide band, β is expected to be large but smaller than L or μ ($\beta \gg 1$ and $\ll L, \mu$ or $\sqrt{J}$). This case corresponds to a strong-coupling band polaron (SCB). We find

$$E_0 = -6J + \frac{3}{2}\beta^2\left(1 - \frac{\beta^2}{8J}\right) - \sqrt{\frac{2}{\pi}}\alpha\beta\left(1 - \frac{\beta^2}{4\mu^2}\right). \tag{21}$$

Minimization gives $\beta_{\min} = \frac{1}{3}\sqrt{2/\pi}\alpha$ and

$$E_0 = -6J - \frac{\alpha^2}{3\pi} + \frac{\alpha^4}{27\pi^2}\left[\frac{1}{\mu^2} - \frac{1}{4J}\right]. \tag{22}$$

In this equation, the first two terms are the usual strong-coupling results of the continuum polaron in the strong-coupling limit while the last term corresponds to corrections to the effective-mass approximation that disappear for an infinitely large band. Note that in this

limit, the polaron radius is proportional to β^{-1}. The polaron stays in this state until its radius becomes of the order of the lattice parameter ($\beta^{-1} \simeq h$ or $\alpha \simeq L$, as $\beta \propto \alpha$ and $L \propto h$). For larger values of α, it becomes self-trapped.

We now consider the narrow-band case for which we expect to find a localized electron (the self-trapped case (ST)). Then, and this is confirmed by numerical calculations, $\beta \to \infty$ and we find

$$E_0 = -\frac{2}{\sqrt{\pi}}\mu\alpha \operatorname{erf}\left(\frac{L}{2\mu}\right) \qquad \left(= -\frac{2}{\pi}\alpha L \quad \text{if} \quad \mu \to \infty\right). \tag{23}$$

This is the Coulomb energy of an electronic charge distributed over a volume of the order of a unit cell in a medium of dielectric constant given by $\left(\varepsilon_\infty^{-1} - \varepsilon_0^{-1}\right)^{-1}$. Note that the term corresponding to the bottom of a tight-binding band ($-6J$) has disappeared, the electron being localized on a lattice site.

It is of interest to derive expressions for the value of α (α_c) at which the ground-state energy of two polaron configurations becomes equal. These expressions, being obtained from asymptotic limits and being compared outside these limits, are expected to give only an indication of the value of the parameters involved for each phase. Surprisingly, in most cases, the resulting numerical results agree quite well with the numerical calculations.

First let us consider the transition between the weak-coupling and the self-trapped phases. The corresponding energies (equations (18) and (23)) are equal at α_{c1}. We get:

$$\alpha_{c1} = 6J \Big/ \left\{ \frac{1}{\sqrt{\pi}} \left[2\mu \operatorname{erf}(L/2\mu) - \int_0^\infty \mathrm{e}^{-t} \frac{\operatorname{erf}\left[L\left(t + 1/4\mu^2\right)^{1/2}\right]}{\left(t + 1/4\mu^2\right)^{1/2}} \, \mathrm{d}t \right] \right\}. \tag{24}$$

For a wide band ($J \gg 1$), this becomes

$$\alpha_{c1} = \frac{6J}{(2/\sqrt{\pi})CG \operatorname{erf}(1/2C)\sqrt{J} - 1}. \tag{25}$$

For a narrow band ($J \ll 1$), and for large values of μ (uniform atomic charge density) we get

$$\alpha_{c1} = \frac{9\pi}{G^3\sqrt{J}}. \tag{26}$$

These values agree with the numerical calculations (next section) in their respective limits.

We define α_{c2} as the value of α for which the polaron passes from a strong-coupling band state to a self-trapped state. It is obtained by equating equations (22) and (23). As the first state is only found for wide bands, we assume that L and μ are large. We then find

$$\alpha_{c2} = 3\sqrt{\pi}G \left[C \operatorname{erf}(1/2C) - \sqrt{C^2 \operatorname{erf}^2(1/2C) - 2/G^2} \right] \sqrt{J}. \tag{27}$$

α_{c2} is thus directly proportional to $\sqrt{J}$ for $J \gg 1$. This expression, as seen in the next section, agrees very well with the numerical calculations.

Finally, we study the transition between the weak-coupling and the strong-coupling band states. This transition occurs at α_{c3} which is obtained by equating equations (19) and (22) in the wide-band limit (keeping L and $\mu \gg 1$). We find

$$\alpha_{c3} = 3\pi. \tag{28}$$

This value does not agree very well with numerical calculations: we show in the next section that, in this limit, the constant is equal to 5.84 instead of 3π as found here. The origin of this discrepancy is that near α_{c3} the minimum value of β is such that neither equation (21) nor equation (22) is valid. This is well known in the continuum polaron

theory and is easily corrected by taking a small-β expansion of equation (13) [15]. We now use numerical calculations to explore the whole parameter space and to validate the asymptotic expansions.

4. Numerical results

The numerical calculations have been done, using equation (13). In this equation, there are three independent parameters: α, J and μ. β is found by minimization and L is related to J by equation (15). In the following calculations, α and J are varied independently. On the other hand, μ is proportional to L since it scales with the inverse of the lattice parameter (see equation (16)). μ^{-1} measures the characteristic length on which an electronic wavefunction of a valence electron decays. In the following, we consider two values for μ: $\mu = L/2$ which is a typical value for a tight-binding solid and $\mu = \infty$ which neglects the variations of the electronic density over an atomic distance. This last value is the same as that used in the continuum approximation but is not equivalent to this approximation since we keep a tight-binding band and a Debye cut-off. This infinite value is used as a comparison and because it gives simpler analytical results. As shown later its use does not qualitatively change the results.

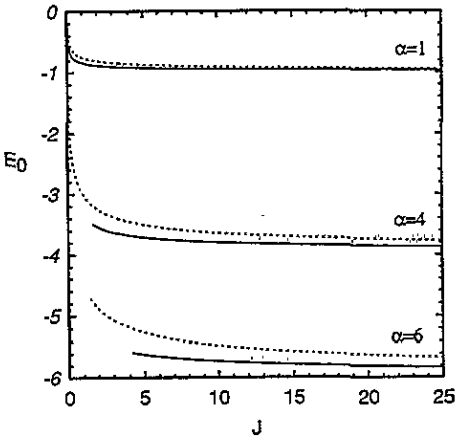

Figure 1. Ground-state energy of the polaron as a function of J, for $\alpha = 1$, 4 and 6. The full-drawn curves are for an infinite value of μ while the dotted ones are for $\mu = L/2$.

We first look at corrections to the continuum approximation. In figure 1, we plot the ground-state energy of the polaron as a function of J, for $\alpha = 1$, 4 and 6 and for $\mu = \infty$ and $L/2$. On this graph, the energies are expressed with respect to the bottom of the conduction band: the $-6J$ term has been subtracted. The curves have been plotted only when the ground state is a band state. Otherwise, nothing has been plotted. The continuum approximation corresponds to the limit of $J \to \infty$. We see that a reduction of the bandwidth has the effect of reducing the self-energy of the band polaron. This effect is more important when the electron–phonon coupling is larger. We note that taking a finite value for μ ($\mu = L/2$) results in a larger reduction of the self-energy of the polaron. Also, self-trapping occurs for larger values of α: the band state is favoured by a modulation of the atomic potential. Note that for most cases of interest ($J \gtrsim 1$), the corrections are small as far as there is no transition to the self-trapped state.

In figures 2 and 3, we present phase diagrams of polaron states in the α–J and α–L

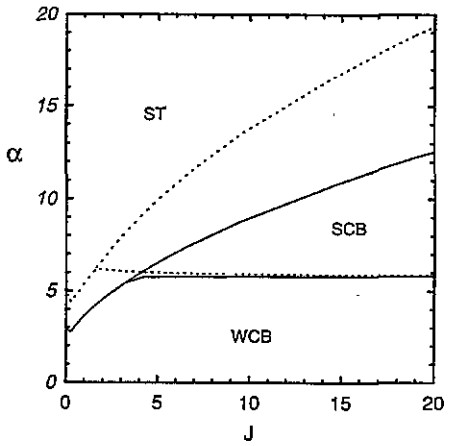

Figure 2. Phase diagram of the tight-binding polaron in the α–J plane. The full-drawn curves are for an infinite value of μ while the dotted ones are for $\mu = L/2$. ST stands for the self-trapped state, WCB for the weak-coupling band state and SCB for the strong-coupling band state.

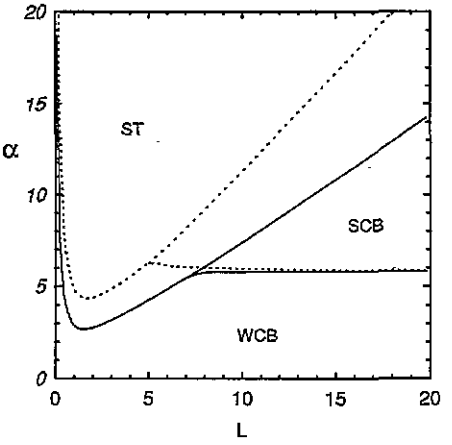

Figure 3. Phase diagram of the tight-binding polaron in the α–L plane. The full-drawn curves are for an infinite value of μ while the dotted ones are for $\mu = L/2$. ST stands for the self-trapped state, WCB for the weak-coupling band state and SCB for the strong-coupling band state.

planes, respectively. These diagrams are obtained by calculating the ground-state energy of the polaron (E_0) for three cases: $E_0(\beta = 0)$ for the weak-coupling band state, $E_0(\beta \to \infty)$ for the self-trapped state and $E_0(\beta = \beta_{\min})$ for the strong-coupling band state. The polaron is then assumed to be in the state of lower energy. The transformation from one state to another is found to occur abruptly, with a region of coexistence of the two states in the neighbourhood of the transition line. In the two diagrams, the full-drawn curves result from taking the limit $\mu \to \infty$ while the dotted curves are plotted for $\mu = L/2$. In the upper part of these graphs, we find a self-trapped state (ST) while in the lower part, a weak-coupling band state (WCB) is found. The intermediate region on the right-hand part of the graphs corresponds to a strong-coupling band state (SCB). These graphs correspond well to the behaviour described by the asymptotic expressions (equations (24)–(28)), the main discrepancy being the value of the horizontal line at $\alpha = 5.84$ which was predicted to be at

3π ($\simeq 10$).

From these figures, we observe that for $\alpha < 2.7$ (or 4.5 for $\mu = L/2$), the polaron is in a weak-coupling band state. Above this value, for small bandwidths, the polaron is in a self-trapped state. For larger bandwidths ($J > 5$), the polaron passes from a weak-coupling to a strong-coupling band state as described by the continuum approximation. For still larger electron–phonon coupling, it passes from a strong-coupling state to a self-trapped state. The span of the strong-coupling part of the diagram increases rapidly with the bandwidth. Note, however, that for real crystals, this strong-coupling part of the diagram cannot be reached since we do not know of any wide-band crystal for which $\alpha > 6$. On the other hand, the self-trapped state can be reached in narrow-band polar materials such as metal oxides or holes in the alkali halides.

One point is questionable in the above analysis: we find that changes in the ground-state configuration of the polaron happen as abrupt transitions between two states when α or J is varied. Also, we find regions in the parameter space for which two energy minima can coexist, one corresponding to the ground state of the polaron and one to a metastable state. These conclusions depend strongly on our use of a variational approach. As an example, it has been shown, in small-polaron theories involving a short-range electron–phonon interaction only, that a Monte Carlo calculation does not agree with an abrupt change between the band state and the self-trapped state. It predicts a continuous change between the two states [9]. However the variational calculations describe correctly the energies of the different states, their dependence on the parameters of the problem and the region of the parameter space for which each state can be found. In the present case, our conclusion is that the above phase diagrams describe adequately the ground-state configuration of the polaron for a given set of parameters. However, the lines appearing on these diagrams are not necessarily related to an abrupt change of polaron state. Another type of approach, such as Monte Carlo calculations, could help in settling this issue.

5. Conclusions

In this paper, we study the tight-binding polaron in a polar material. Our purpose is to characterize the polaron in cases where the continuum approximation is not valid. This is the case when the size of the lattice deformation becomes of the order of size of the unit cell. Because of the resulting spatial confinement, the electron increases its kinetic energy and the effective-mass approximation is no longer valid. We take care of this aspect by going back to the original electronic Hamiltonian involving an electron in interaction with a periodic lattice potential. Furthermore, the electron localization cannot be smaller than a distance of the order of the lattice parameter. A Debye cut-off takes this effect into account. Thus the resulting Hamiltonian has the Fröhlich form with two corrections: a Debye cut-off on the phonon wavevectors and the addition of the lattice potential.

This Hamiltonian is then treated in a tight-binding spirit. We first write it in a tight-binding representation. Then, we calculate an upper bound to the ground-state energy of the polaron using the Fock approximation of Matz and Burkey [12]. The resulting energy is valid in both the adiabatic and non-adiabatic limits, for any value of electron–phonon coupling constant (α). Well known results obtained from theories based on the continuum approximation can be derived as special cases of our formalism, in the wide-band limit.

Using this formalism, we find the following results. First, for large bandwidths, we obtain a polaron behaviour similar to that obtained from the continuum approximation: for small electron–phonon coupling, we find a weak-coupling band state consisting of a delocalized polaron in a band state while, for larger coupling, we find a strong-coupling

band polaron consisting in a polaron with an internal structure moving in a narrow band. For these two states, the corrections to the continuum approximation are found to be small. For still larger coupling, when the radius of the polaron becomes of the order of the lattice parameter, we find a self-trapped state consisting in a trapped electron whose wave-function is localized on a lattice site. Second, in the opposite limit (for small bandwidths), we do not find a strong-coupling band state: the polaron passes directly from the weak-coupling band state to the self-trapped state when the electron–phonon coupling increases. These results are summarized as phase diagrams in the preceding section.

From these phase diagrams, we draw the following conclusions concerning the different polaron states. In wide-band materials, we expect to find weak-coupling band polarons well described by the continuum approximation. This is the case of III–V and II–VI compounds and of electrons in alkali halides. In this limit, we cannot find any crystal for which α, the electron–phonon coupling constant, is larger than six. We thus conclude that the strong-coupling band polaron cannot be found in these crystals. This is consistent with previous works where the same conclusion was found, within the continuum approximation, using the Feynman path-integral formalism [16]. On the other hand, for narrow-band materials, one can find larger values for the electron–phonon coupling constant. This is the case for electrons in metal oxides and in perovskites. However, because of the small bandwidth, the polaron passes directly from a weak-coupling band state to a self-trapped state, as can be seen on the phase diagrams (figures 2 and 3). The strong-coupling band state does not exist in this limit. We are thus led to conclude that this state cannot be observed at all in real crystals.

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