Polarons

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Abstract

A conduction electron (or hole) together with its self-induced polarization in a polar semiconductor or an ionic crystal forms a quasiparticle, which is called a polaron. The polaron concept is of interest, not only because it describes the particular physical properties of charge carriers in polarizable solids but also because it constitutes an interesting field theoretical model consisting of a fermion interacting with a scalar boson field. The early work on polarons was concerned with general theoretical formulations and approximations, which now constitute the standard polaron theory and with experiments on cyclotron resonance and transport properties. Because of the more recent interest in the two-dimensional electron gas, the study of the polaron in two dimensions became important. Again cyclotron resonance, and therefore the behaviour of polarons in magnetic fields, was a key issue. When two electrons (or two holes) interact with each other simultaneously through the Coulomb force and via the electron-phonon-electron interaction, either two independent polarons can occur or a bound state of two polarons — a bipolaron — can arise. Bipolarons have been considered to possibly play a role in high-T_C superconductivity. Originally the polaron was mainly studied to describe the polar interaction between an electron and the longitudinal optical phonons. The polaron concept has been extended to several systems where one or many fermions interact with a bath of bosons, e. g.,

- small polaron,
- piezopolaron,
- polaronic exciton,
- spin — or magnetic — polaron,
- “ripplonic polaron”,
- “plasmaron”,
- “hydrated polarons”,
- electronic polaron

etc. Polarons in conducting polymers and in fullerenes also constitute an emerging subject.

Introduction

The polaron concept is of interest, not only because it describes the particular physical properties of an electron in polar crystals and ionic semiconductors but also because it is an interesting field theoretical model consisting of a fermion interacting with a scalar boson field.

The early work on polarons was concerned with general theoretical formulations and approximations, which now constitute the standard theory and with experiments on cyclotron resonance and transport properties.

Because of the more recent interest in the two-dimensional electron gas (2DEG) the study of the polaron in two dimensions became important. A cyclotron resonance, and therefore the behaviour of polarons in magnetic fields, was a key issue.

1 The Polaron Concept and the Fröhlich Polaron

1.1 The concept

A conduction electron (or hole) together with its self-induced polarization in a polar semiconductor or an ionic crystal forms a quasiparticle, which is called a *POLARON* (Fig. 1). The physical properties of the polaron differ from those of the band-electron. In particular the polaron is characterized by its binding or (self-) energy, effective mass and by its response to external electric and magnetic fields (e. g. mobility and impedance). The general polaron concept was introduced by Landau (1933) in a paper of about one page. Subsequently Landau and Pekar [see (Pekar, 1951)] investigated the self-energy and the effective mass of the polaron, for what was shown by Fröhlich (1954) to correspond to the adiabatic or strong-coupling regime.

The early work on polarons was devoted to the interaction between a charge carrier (electron, hole) and the long-wavelength optical phonons. The (now standard) field-theoretical Hamiltonian describing this interaction was derived by Fröhlich:

$$H = \frac{\mathbf{p}^2}{2m_b} + \sum_{\mathbf{k}} \hbar\omega_{LO} a^{+}_{\mathbf{k}} a_{\mathbf{k}} + \sum_{\mathbf{k}} (V_k a_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} + h.c.), \qquad (1a)$$

where $\mathbf{r}$ is the position coordinate operator of the electron with band mass m_b, $\mathbf{p}$ is its canonically conjugate momentum operator; $a^{\dagger}_{\mathbf{k}}$ and $a_{\mathbf{k}}$ are the creation (and annihilation) operators for longitudinal optical phonons of wave vector $\mathbf{k}$ and energy $\hbar\omega_{LO}$. The V_k are Fourier components of the electron-phonon interaction

$$V_k = -i\frac{\hbar\omega_{LO}}{k}\left(\frac{4\pi\alpha}{V}\right)^{\frac{1}{2}}\left(\frac{\hbar}{2m_b\omega_{LO}}\right)^{\frac{1}{4}}, \qquad (1b)$$

$$\alpha = \frac{e^2}{\hbar c}\sqrt{\frac{m_b c^2}{2\hbar\omega_{LO}}}\left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}\right) \qquad (1c)$$

α is called the Fröhlich coupling constant, ε_∞ and ε_0 are respectively the electronic and the static dielectric constant of the polar crystal. In Table 1 a list is given of the coupling constants for a number of crystals.

In deriving the form of V_k, Eqs. (1b) and (1c), it was assumed that (i) the spatial extension of the polaron is large compared to the lattice parameters of the solid ("continuum" approximation), (ii) spin and relativistic effects can be neglected, (iii) the band-electron has parabolic dispersion, (iv) in conjunction with the first approximation it is also assumed that the LO-phonons of interest for the interaction, are the long-wavelength phonons with constant frequency ω_{LO}.

The original concept of the polaron, as discussed above, has been generalized over the years to include polarization fields other than the LO-phonon field: the acoustical phonon field, the exciton field, etc. .... For some materials the continuum approximation is not appropriate as far as the polarization is confined to a region of the order of a unit cell; the so-called "small polaron" is a more adequate quasiparticle in that case (see section 2).

It is customary to use the term "Fröhlich-polaron" or "large polaron" for the quasiparticle consisting of the electron (or hole) and the polarization due to the LO-phonons. The term Landau- or Pekar- or Landau-Fröhlich-polaron would be more appropriate.

In this first section the properties of Fröhlich polarons are reviewed; other realisations of the polaron concept (small polarons, spin polarons etc...) are discussed in later sections. For the reviews on polarons see Kuper and Whitfield (1963), Appel (1968), Devreese (1972), Devreese and Peeters (1984).

1.2 Standard Fröhlich-polaron theory. Self energy and effective mass of the polaron

Historically the first studies on polarons [the "Russian work": Landau (1933), Pekar (1951)] were based on a "Produkt-Ansatz" for the polaron wave-function

$$|\Phi\rangle = |\Psi(\mathbf{r})\rangle|\text{field}\rangle = |\Psi(\mathbf{r})\rangle|f\rangle \qquad (2a)$$

where $|\Psi(\mathbf{r})\rangle$ is the electron-wave function. The field wave function parametrically depends on the electron wave function. Fröhlich showed that the approximation (2a) leads to results which are only valid as $\alpha \to \infty$ (the strong-coupling regime). It should be pointed out that a more systematic analysis of the strong-coupling polarons based on canonical transformations of the Hamiltonian (1a) was performed in pioneering investigations by Bogolubov (1950), Bogolubov and Tyablikov (1949), Tyablikov (1951).

Fröhlich also found that Eq. (2a) is a poor Ansatz to represent actual crystals which have α-values typically ranging from $\alpha = 0.02$ (InSb) to $\alpha \sim 3$ to 4 (alkali halides). This work showed the need for a weak-coupling theory of the polaron which in fact was provided originally by Fröhlich (1954). However it turns out that for $\alpha \approx 3$ perturbation expansions in powers of α are not always sufficient; therefore an intermediate-coupling or — better — an all-coupling theory was necessary.

In what follows the key concepts of the standard Fröhlich-polaron theories are reviewed.

1.2.1 Strong coupling

The Produkt-Ansatz (2a) — or Born-Oppenheimer approximation — implies that the electron adiabatically follows the motion of the atoms (Pekar, 1951). With the use of the canonical transformation

$$S = \exp\left[-\sum_{\mathbf{k}}\left(\frac{V_k^* \rho_{\mathbf{k}}^*}{e\hbar\omega_{LO}} a_{\mathbf{k}} - h.c.\right)\right], \qquad (2b)$$

where

$$\rho_{\mathbf{k}} = e < \Psi(\mathbf{r})|e^{i\mathbf{k}\cdot\mathbf{r}}|\Psi(\mathbf{r}) >, \qquad (2c)$$

it leads to $|f\rangle = S|0\rangle$. The ket $|0\rangle$ describes the vacuum state. With Eqs. (2) and a Gaussian trial function for $|\Psi(\mathbf{r})\rangle$, the groundstate energy of the polaron E_0 (calculated with the energy of the uncoupled electron-phonon system as zero energy) takes the form:

$$E_0 = -\frac{\alpha^2}{3\pi}\hbar\omega_{LO} = -0.106\alpha^2\hbar\omega_{LO}. \quad (3a)$$

At strong coupling, the polaron is characterized by Franck-Condon (F. C.) excited states, which correspond to excitations of the electron in the potential adapted to the groundstate. The energy of the lowest F. C. state is, within the Produkt-Ansatz:

$$E_{FC} = \frac{\alpha^2}{9\pi}\hbar\omega_{LO} = 0.0354\alpha^2\hbar\omega_{LO}. \quad (3b)$$

If the lattice polarization is allowed to relax or adapt to the electronic distribution of the excited electron (which itself then adapts its wave function to the new potential, etc. …leading to a self-consistent final state), the so-called relaxed excited state (R. E. S.) results (Pekar, 1951). Its energy is (Evrard, 1965; Devreese, Evrard, 1966):

$$E_{RES} = -0.041\alpha^2\hbar\omega_{LO}. \quad (3c)$$

In fact, both the F. C. state and the R. E. S. lie in the continuum [1] and, strictly speaking, are resonances (Fig. 2).

The strong-coupling mass of the polaron, resulting again from the approximation (2), is given as:

$$\frac{m^*}{m_b} = 1 + 0.0200\alpha^4. \quad (3d)$$

More rigorous strong-coupling expansions for E_0 and m^* have been presented in the literature (Miyake, 1975):

$$\frac{E_0}{\hbar\omega_{LO}} = -0.108513\alpha^2 - 2.836, \quad (4a)$$

$$\frac{m^*}{m_b} = 1 + 0.0227019\alpha^4. \quad (4b)$$

The main significance of the strong-coupling theory is that it allows to test "all-coupling" theories in the limit $\alpha \to \infty$. From the formal point of view a deeper study of the status and uniqueness of the strong-coupling solutions was undertaken by Lieb (1977).

1.2.2 Weak coupling

Fröhlich (1954) has provided the first weak-coupling perturbation-theory results:

$$E_0 = -\alpha\hbar\omega_{LO} \quad (5a)$$

and

$$m^* = \frac{m_b}{1 - \alpha/6}. \quad (5b)$$

Inspired by the work of Tomonaga, Lee *et al.* (1953) (usually cited as L. L. P.) have derived (5a) and $m^* = m_b(1 + \alpha/6)$ from an elegant canonical transformation formulation. In fact, they perform two successive canonical transformations:

$$S_1 = \exp\left[\frac{i}{\hbar}(\mathbf{P} - \sum_{\mathbf{k}} \hbar\mathbf{k} a_{\mathbf{k}}^\dagger a_{\mathbf{k}})\cdot\mathbf{r}\right], \quad (6a)$$

where $\mathbf{P}$ is the polaron total-momentum operator. The canonical transformation (6a) formally eliminates the electron operators from the Hamiltonian.

The second canonical transformation is of the "displaced-oscillator" form:

$$S_2 = \exp\left[\sum_{\mathbf{k}} (a_{\mathbf{k}}^\dagger f_{\mathbf{k}} - a_{\mathbf{k}} f_{\mathbf{k}}^*)\right]. \quad (6b)$$

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[1] The R. E. S. lies in the continuum of so-called scattering states, not indicated in the figure.

The $f_{\mathbf{k}}$ are treated as variational functions. The physical significance of Eq. (6b) is that it "dresses" the electron with the virtual phonon field which describes the polarization.

The L. L. P. approximation has often been called "intermediate-coupling theory". However its range of validity is in principle not larger than that of the weak-coupling approximation. The main significance of the L. L. P. approximation, is in the elegance of the canonical transformations S_1 and S_2, together with the fact that it puts the Fröhlich result on a variational basis.

In his basic article on polarons, Feynman (1955) found the following higher-order weak-coupling expansions:

$$\frac{E_0}{\hbar\omega_{LO}} = -\alpha - 0.0123\alpha^2 - 0.00064\alpha^3 - \ldots \ (\alpha \to 0), \quad (7a)$$

$$\frac{m^*}{m_b} = 1 + \frac{\alpha}{6} + 0.025\alpha^2 + \ldots \ (\alpha \to 0). \quad (7b)$$

Since then a lot of theoretical work was devoted to obtain more exact coefficients in this expansion. Höhler and Müllensiefen (1959) calculated the coefficients for α^2 to be -0.016 in the energy and 0.0236 in the polaron mass. Röseler (1968) found the analytical expressions for the above-mentioned coefficients: $2\ln(\sqrt{2}+1) - \frac{3}{2}\ln 2 - \frac{\sqrt{2}}{2} \approx -0.01591962$ and $\frac{4}{3}\ln(\sqrt{2}+1) - \frac{2}{3}\ln 2 - \frac{5\sqrt{2}}{8} + \frac{7}{36} \approx 0.02362763$, respectively. At present the following most accurate higher-order weak-coupling expansions are known: for the energy (Smondyrev, 1986; Selyugin and Smondyrev, 1989)

$$\frac{E_0}{\hbar\omega_{LO}} = -\alpha - 0.0159196220\alpha^2 - 0.000806070048\alpha^3 - \ldots, \quad (7c)$$

and for the polaron mass (Röseler, 1968)

$$\frac{m^*}{m_b} = 1 + \frac{\alpha}{6} + 0.02362763\alpha^2 + \ldots, \quad (7d)$$

which are a striking illustration of the heuristical value of Feynman's path-integral approach in the polaron theory.

1.2.3 All-coupling theory. Feynman path integral.

In the early fifties H. Fröhlich gave a seminar at Caltech. In this seminar he discussed the weak-coupling polaron mass as derived by him: $m^* = m_b/(1 - \alpha/6)$. He suggested that, if the electron-phonon coupling could be accurately treated for intermediate coupling (in particular around $\alpha \approx 6$) this might lead to new insights in the theory of superconductivity (this was before BCS) (Feynman, 1973). Feynman was among the audience. He went to the library to study one of Fröhlich's papers on polarons, (Fröhlich, 1954). There he got the idea to formulate the polaron problem into the Lagrangian form, of quantum mechanics and then eliminate the field oscillators, "…in exact analogy to Q. E. D. …(resulting in) …a sum over all trajectories …". The resulting path integral is of the form (Feynman, 1955):

$$\langle 0,\beta|0,0\rangle = \int \mathcal{D}\mathbf{r}(\tau)\exp\left[-\frac{1}{2}\int_0^\beta \dot{\mathbf{r}}^2 d\tau + \frac{\alpha}{2^{\frac{3}{2}}}\int_0^\beta\int_0^\beta \frac{e^{-|\tau-\sigma|}}{|\mathbf{r}(\tau)-\mathbf{r}(\sigma)|}d\tau d\sigma\right], \quad (8a)$$

where $\beta = 1/(k_B T)$. This path integral (8a) has a great intuitive appeal: it shows the polaron problem as an equivalent one-particle problem in which the interaction, non-local in time or "retarded", is between the electron and itself. Subsequently Feynman showed (in fact to M. Baranger) how the variational principle of quantum mechanics could be adapted to the path integral and introduced a quadratic trial action (again non-local in time) to simulate Eq. (8a).

It may be noted, that the elimination of the phonon field (or the boson field in general) introduced through Eq. (8a) by Feynman has found many applications, e. g. in the study of dissipation phenomena

Applying the variational principle for path integrals resulted in an upper bound for the polaron self-energy at all α, which at weak and strong coupling gave accurate limits. Feynman obtained the smooth interpolation between weak and strong coupling (for the groundstate energy). It is worthwhile to give the asymptotic expansions of Feynman's polaron theory. In the weak-coupling limit, they are given above by Eqs. (7a) and (7b). In another — strong-coupling limit — Feynman found for the energy:

$$\frac{E_0}{\hbar\omega_{LO}} \equiv \frac{E_{3D}(\alpha)}{\hbar\omega_{LO}} = -0.106\alpha^2 - 2.83 - \ldots \quad (\alpha\to\infty). \quad (9a)$$

and for the polaron mass:

$$\frac{m^*}{m_b} \equiv \frac{m^*_{3D}(\alpha)}{m_b} = 0.0202\alpha^4 + \ldots \quad (\alpha\to\infty). \quad (9b)$$

Over the years the Feynman model for the polaron has remained in many respects the most successful approach to this problem. It is also remarkable that, despite several efforts, no equivalent Hamiltonian formulation of this path integral approach has been realised. [In one case (Yamazaki, 1983) the formal structure of the theory was reobtained in a Hamiltonian formulation—be it very artificial—but no variational principle leading to an upper bound for the energy could be found.] The theory of polarons in semiconductors with degenerate bands and of statistical ensembles of polarons, related to many-polaron problems, is reviewed from the unified point of view of the path integration over the Wick symbols by Fomin and Pokatilov (1988).

1.2.4 Response properties of Fröhlich polarons. Mobility and optical properties

The transport properties of polar and ionic solids are influenced by the polaron coupling. Intuitively one expects that the mobility of large polarons will be inversely proportional to the number of real phonons present in the crystal:

$$\mu \sim \mathrm{e}^{\hbar\omega_{LO}/kT}. \quad (10a)$$

The first to point out the typical behaviour (characteristic for weak coupling) of Eq. (10a) was Fröhlich (1937). Kadanoff (1963) provided a derivation of the weak-coupling, low-temperature mobility starting from the Boltzmann equation; his result is

$$\mu = \frac{4}{3\pi^{1/2}} \frac{e}{m^* \alpha \omega_{LO}} G(z) \mathrm{e}^{\hbar\omega_{LO}/kT} \left(\frac{kT}{\hbar\omega_{LO}} \right)^{1/2}, \quad (10b)$$

where $G(z)$, defined by Howarth and Sondheimer (1953), is of order 1.

Feynman *et al.* (1962) (usually referred to as F. H. I. P.) have elaborated a framework allowing the analysis of the response properties of a system, using path integrals. For low temperatures they obtain the following expression for the dc mobility:

$$\mu \equiv \mu_{3D}(\alpha) = \frac{e}{2m^* \omega_{LO} \alpha} \frac{3}{2} \left(\frac{w}{v} \right)^3 \exp\left(\frac{v^2 - w^2}{w^2 v} \right) \mathrm{e}^{\hbar\omega_{LO}/kT} \frac{kT}{\hbar\omega_{LO}}, \quad (10c)$$

where w, v are functions of α (also adequate for large α) deriving from the Feynman polaron model[2]. For the impedance of a polaron $Z(\nu) \equiv Z_{3D}(\alpha, \nu)$ describing its response to the ac electric field of frequency ν, see Feynman *et al.* (1962).

Equation (10c) and related approximations allowed to explain the experimental results of Brown and his co-workers [see (Brown, 1963)] on alkali halides and silver halides, see e. g. Fig. 3, in the temperature region where the electron-LO-phonon scattering is the dominant process (at low temperatures $T < 50$K the impurity scattering starts to prevail). Equation (10c) presupposed a "drifted-Maxwellian" velocity distribution of the polarons; this limits the validity of the treatment theoretically. However, because other scattering mechanisms than LO-phonon scattering might "conspire" to induce a Maxwellian distribution, the range of validity of Eq. (10c) seems to be larger than one would expect from electron-LO-phonon interaction only. A review on the mobility of Fröhlich polarons, written from a unified point of view, was presented by Peeters and Devreese (1984).

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[2] It is noted that a misprint occurred in this formula in the *Encyclopedia of Physics* (Lerner, Trigg, 1991).

It was shown by the author and his co-authors [see (Devreese, 1972)] how the optical absorption of Fröhlich polarons, for all coupling, can be calculated starting from the F. H. I. P.-scheme (which gives a derivation for the impedance function). This work led to the following expression for the optical absorption:

$$\Gamma(\nu) \sim \frac{\mathrm{Im}\Sigma(\nu)}{[\nu - \mathrm{Re}\Sigma(\nu)]^2 + [\mathrm{Im}\Sigma(\nu)]^2}, \quad (10d)$$

where ν is the frequency of the incident radiation, $\Sigma(\nu)$ is the so-called "memory function" which contains the dynamics of the polaron and depends on α and ν.

As an example, in Fig. 4 the optical absorption spectrum of Fröhlich polarons for $\alpha = 6$ is shown.

It is remarkable that from (10d) in (Devreese, 1972) the three different kinds of polaron excitations, studied before only in asymptotic limits, are seen to appear in the spectra:

- a) scattering states where e. g. one real phonon is excited (the structure starting at $\nu = 1$);
- b) R. E. S. (Kartheuser *et al.*, 1969; Evrard, 1965);
- c) F. C. states (Kartheuser *et al.*, 1969; Evrard, 1965).

Experimentally only the "scattering states" have been seen for free polarons (Finkenrath *et al.*, 1969); the R. E. S. might play a role for bipolarons (Verbist *et al.* 1994). However, the full structure of Eq. (10d) has been revealed through cyclotron resonance measurements for which $\nu - \mathrm{Re}\Sigma(\nu)$ is replaced by $\nu - \omega_c - \mathrm{Re}\Sigma(\nu)$ so that the resonance conditions can be tuned by changing ω_c.

The weak-coupling limit of Eq. (10d) coincides with the results by Gurevich *et al.* (1962), whereas the structure of the strong-coupling limit confirms the identification of the internal polaron excitations by Kartheuser *et al.* (1969).

In pioneering experimental studies Brown and co-workers [see (Brown, 1963)] have combined mobility experiments and cyclotron resonance measurements to clearly demonstrate the polaron effect. From a theoretical plot of mobility versus band mass in AgBr compared to experimental mobility data at a given temperature, they estimate the band mass. This allows to calculate α and the polaron mass m^*. This value of m^* can then be compared to the measured cyclotron mass. The experimental value $m^*/m_b = 0.27 \pm 0.01$ is obtained for AgBr at 18 K to be compared to a theoretical value $m^*/m_b = 0.27 \pm 0.05$.

1.3 Fröhlich polarons in 2D

1.3.1 Introduction

Today electron systems in reduced dimensions e. g. in two dimensions like in GaAs-AlGaAs or MOSFETS are of great interest. Also the electron-phonon interaction and the polaron effect in such systems receive much attention. For one polaron, confined to two dimensions, but interacting with a 3D phonon gas, the Fröhlich Hamiltonian remains of the form (1a) with the following modification for the V_k (Peeters *et al.*, 1986a):

$$V_k = -i\hbar\omega_{LO}\left(\frac{\sqrt{2}\pi\alpha}{Ak}\right)^{\frac{1}{2}}\left(\frac{\hbar}{m_b\omega_{LO}}\right)^{\frac{1}{4}}, \quad (11)$$

valid because of the fact that the electron-polarization interaction is of the standard form $1/r$ in an arbitrary number of space dimensions. A possible dependence of the electron-phonon interaction on a concrete physical mechanism of the electron confinement to two dimensions was considered by Fomin and Smondyrev (1994). The self-energy $\Delta E/\hbar\omega_{LO}$ for a polaron in $2D$ for $\alpha \to 0$ and $\alpha \to \infty$ were derived by Xiaoguang *et al.* (1985), Das Sarma and Mason (1985):

$$\frac{\Delta E}{\hbar\omega_{LO}} \equiv \frac{E_{2D}(\alpha)}{\hbar\omega_{LO}} = -\frac{\pi}{2}\alpha - 0.06397\alpha^2 + O(\alpha^3) \ \ (\alpha \to 0), \quad (11a)$$

$$\frac{\Delta E}{\hbar\omega_{LO}} \equiv \frac{E_{2D}(\alpha)}{\hbar\omega_{LO}} = -0.4047\alpha^2 + O(\alpha^0) \ \ (\alpha \to \infty). \quad (11b)$$

The corresponding results for the polaron mass in 2D are [Xiaoguang *et al.* (1985)]:

$$\frac{m^*}{m_b} \equiv \frac{m^*_{2D}(\alpha)}{m_{2D}} = \frac{\pi}{8}\alpha + 0.1272348\alpha^2 + O(\alpha^3) \ \ (\alpha \to 0), \quad (11c)$$

$$\frac{m^*}{m_b} \equiv \frac{m^*_{2D}(\alpha)}{m_{2D}} = 0.733\alpha^4 + O(\alpha^2) \ \ (\alpha \to \infty). \quad (11d)$$

The result $\Delta E/\hbar\omega_{LO} = -(\pi/2)\alpha$ was first obtained by Sak (1972).

1.3.2 Scaling relations

Peeters and Devreese (1987) have derived several scaling relations connecting the polaron self-energy, the effective mass, the impedance Z and the mobility μ in $2D$ to the same quantities in $3D$. Those relations were derived on the level of the Feynman approximation and are listed here:

$$E_{2D}(\alpha) = \frac{2}{3}E_{3D}\left(\frac{3\pi}{4}\alpha\right), \quad (12a)$$

$$\frac{m^*_{2D}(\alpha)}{m_{2D}} = \frac{m^*_{3D}\left(\frac{3\pi}{4}\alpha\right)}{m_{3D}}, \quad (12b)$$

$$Z_{2D}(\alpha,\nu) = Z_{3D}\left(\frac{3\pi}{4}\alpha,\nu\right), \quad (12c)$$

where ν is the frequency of the external electromagnetic field, and

$$\mu_{2D}(\alpha) = \mu_{3D}\left(\frac{3\pi}{4}\alpha\right). \quad (12d)$$

Except for the investigations on polarons at the surface of liquid He (Jackson, Platzman, 1981; Devreese, Peeters, 1987), the experimental studies performed at present, are related to systems with weak electron-phonon coupling. Those studies have addressed a variety of physical properties including magneto-phonon anomalies, optical absorption, plasmon-LO-phonon mode coupling, cyclotron resonance, mobility, many-body effects, etc. ...The reader is referred to (Devreese, Peeters, 1987) for more details and additional references. In what follows some of these studies will be further discussed.

1.4 Fröhlich Polarons in a magnetic field

1.4.1 In 3D

Fröhlich polarons have been most clearly manifested by investigations of their properties in magnetic fields. Therefore a special section is devoted to the study of polarons in magnetic fields.

1.4.1.1. Level crossing, pinning. In interpreting the (low field) cyclotron resonance experiment of Brown *et al.* it was supposed that the zero-magnetic-field polaron mass is observed.

Of course there exists no *a priori* guarantee that this supposition is true and theoretical studies of polarons in magnetic fields are necessary. Larsen (1972, 1991) has made important contributions to the theoretical study of polarons in magnetic fields. In particular he was the first to point out the level repulsion close to the crossing of levels at $\omega_c = \omega_{LO}$ (ω_c is the cyclotron resonance frequency) and the pinning of Landau levels to the phonon continuum as $\omega_c \to \infty$ (see Fig. 5). Measurements on InSb (Johnson, Larsen, 1966) and CdTe (Waldman *et al.*, 1969) provided first indications for these level crossing and pinning phenomena. Detailed lineshape studies for weak coupling of the cyclotron resonance, revealing a double peak structure close to $\omega_c = \omega_{LO}$, are displayed by Vigneron *et al.* (1978) and independently by Van Royen and Devreese (1981).

1.4.1.2. Static and dynamic properties of polarons in a magnetic field. Peeters and Devreese (1982) have generalized the Feynman model of the polaron to the case where a static external magnetic field is applied. The calculation is valid for all α, ω_c and temperature described by the parameter β. The starting point is the expression of the free energy of the polaron as a path integral

$$F = F_{ph} - \frac{1}{\beta} \ln \left\{ \int d\mathbf{r} \int_{\mathbf{r}(0)=\mathbf{r}}^{\mathbf{r}(\beta)=\mathbf{r}} \mathcal{D}\mathbf{r}(u) \exp(S[r(u)]) \right\} . \quad (13a)$$

The "electron" contribution to the action S is

$$S_e = -\frac{1}{2} \int_0^\beta du[\dot{\mathbf{r}}(u)^2 + i\omega_c(x(u)\dot{y}(u) - y(u)\dot{x}(u))], \quad (13b)$$

where $\mathbf{r}$ is the position vector of the electron, with components x, y in the plane perpendicular to the magnetic field.

A quadratic, retarded model interaction was introduced (Peeters, Devreese, 1982) to simulate the polaron (retarded Coulomb) interaction and, in analogy to the zero-magnetic field case, the Jensen-Feynman inequality was used:

$$F \leq F_{ph} + F_m - \frac{1}{\beta} < S - S_m >_m . \quad (13c)$$

Here F_{ph}, F_m stand for the free energy of the phonon bath and the quadratic model respectively, while $< \cdot >_m$ denotes an evaluation of the corresponding average with

$$\mathrm{e}^{S_m} / \int d\mathbf{r} \int_{\mathbf{r}(0)=\mathbf{r}}^{\mathbf{r}(\beta)=\mathbf{r}} \mathcal{D}\mathbf{r}(u) \mathrm{e}^{S_m} \quad (13d)$$

as weight factor. For details the reader is referred to (Peeters, Devreese, 1982), where results for the energy and related properties of the polaron in a magnetic field for all α, ω_c, β were derived both numerically and — in a variety of limiting cases — analytically.

A question of considerable significance raised about the validity of the inequality (13c) in the presence of a magnetic field. Feynman suggested that in a magnetic field this inequality remains valid, or might need a slight modification only (Feynman, Hibbs, 1965). Several works have been devoted to this challenging problem, see (Brosens, Devreese, 1988), Sec. 3.4 in (Fomin, Pokatilov, 1988), and (Larsen, 1991) for a detailed review. Larsen (1985) revealed that the groundstate levels of a 2D-polaron obtained variationally on the basis of (13c) for sufficiently high magnetic fields lie below those found within the framework of the adiabatic strong-coupling theory or the fourth-order perturbation weak-coupling approach. Interpreting the latter groundstate level as the exact one, Larsen came to the conclusion that it would seem difficult to attach any particular sense to the variational groundstate level.

It is worthwhile that the perturbation groundstate energy can however itself be treated in some cases [see (Fomin, Pokatilov, 1988), *loc. cit.*] as an upper bound for the exact energy. But when comparing various upper bounds for the exact energy, one should recall Feynman's (1955) warning that attempts to improve an upper bound by calculating the higher-order correction terms may indeed deprive the treatment of its variational nature! Using a model calculation, Brosens and Devreese (1988) rigorously demonstrated that for sufficiently small electron-phonon coupling the presence of a magnetic field is prohibitive for the application of the Jensen-Feynman inequality.

A generalization of the Jensen-Feynman inequality, which remains valid in the case of a nonzero magnetic field, was derived by Devreese and Brosens (1992) starting from the ordered operator calculus. On these grounds, the conditions were determined to be imposed on the variational parameters in the model action S_m, such that the Feynman upper bound in its original form of the inequality (13c) remains valid for a polaron in a magnetic field. Although sofar it has not been conclusively established that a choice of the parameters in the trial action made in (Peeters, Devreese, 1982) limits them to the domain determined by the conditions derived in the above-cited work, it is interesting to note that most of the existing theories of polarons in a magnetic field (Hellwarth, Platzman, 1962; Marshall, Chawla, 1970; Evrard *et al.*, 1970; Lépine, Matz, 1976) are obtained as special cases of the results by Peeters and Devreese (1982) who simply accepted the inequality (13c) as the working hypothesis. A prediction by Peeters and Devreese (1982) is that some quantities characterizing the internal structure of the polaron (called e. g. $(v_\perp/w_\perp)^2$ in the mentioned paper) undergo a drastic change for a well-defined magnetic field ("stripping transition"). Although high magnetic fields are needed (e. g., ~ 42 T in AgBr), it would be interesting to investigate this point experimentally.

1.4.1.3. Cyclotron resonance spectra. The observation of the cyclotron mass of electrons in AgBr in the low field case ($\omega_c \to 0$) gave evidence for the occurrence of polaron effects. However it concerns only one number (m^*/m_e) and involves the combination of two measurements (m_e is the mass of the electron in vacuum).

It would therefore be useful to analyze the magnetic field dependence of the polaron mass in order to gain quantitative insight into the validity of the polaron picture.

An excellent occasion to realize such an analysis is provided by the, more recent, precise cyclotron mass measurements (in AgBr and AgCl) by Hodby *et al.* (1987). These measurements, performed with the 5 cm bore hybrid magnet at Oxford, cover the range from zero magnetic field to 16 T. These measurements are precise enough to distinguish between various polaron theories. Several theories were compared in analyzing the experimental data of by Hodby *et al.* (1987).

First, the variational calculation of Larsen (1972) was considered. This approach is a so-called intermediate-coupling theory to calculate the energy levels (modified Landau levels) of a polaron in a magnetic field. The polaron mass is then defined from the energy differences between the polaron (Landau-) energy levels.

In principle, it is better to calculate the magneto-optical absorption spectrum of the polaron (the quantity which is actually measured) and to define the polaron mass, in the same way as the experimentalist, from the peak positions in the spectrum. Starting from the results of Peeters and Devreese (1982), the magneto-optical absorption of polarons for all α and ω_c at $T = 0$ was calculated by Peeters and Devreese (1986). They evaluated the memory-function formalism to generalize the study of the response of a Feynman polaron in a magnetic field. The magneto-absorption is then obtained from

$$\lim_{\varepsilon \to 0} \frac{1}{\nu - \omega_c - \sum(\nu + i\varepsilon)}, \quad (14a)$$

where ν is the frequency of the incident radiation and $\sum(\nu + i\varepsilon)$ is the memory-function. The key ingredient of $\sum(\nu + i\varepsilon)$ is the space Fourier transform of the density-density correlation function:

$$< e^{i\mathbf{k}\cdot\mathbf{r}(t)} e^{-i\mathbf{k}\cdot\mathbf{r}(0)} >, \quad (14b)$$

where $< \cdot >$ can be expressed as a path integral. $\sum(\nu + i\varepsilon)$ is an intricate function which takes into account all the polaron internal states and all the Landau levels. It turns out that the magneto-absorption calculated by Peeters and Devreese (1986) leads to the best quantitative agreement between theory and experiment as was analyzed for AgBr and AgCl (Hodby *et al.*, 1987). It should be pointed out that the weak-coupling theories (Rayleigh-Schrödinger perturbation theory, Wigner-Brillouin one and its improvements) fail (and are all off by at least 20% at 16 T) to describe the experimental data for the silver halides. The analysis of Hodby *et al.* (1987) provides a confirmation of the Fröhlich description of the polaron in a case where weak-coupling approximations are adequate.

An interesting case is provided by the cyclotron resonance data for CdTe (Johnson, Larsen, 1966). The early analysis (Larsen, 1972) of these experiments as well as subsequent cyclotron-resonance measurements of the polaron effective mass in n-CdTe (Litton *et al.*, 1976) seemed to suggest that the Fröhlich coupling constant as large as $\alpha = 0.4$ could explain the data for the polaron mass as a function of magnetic field. This gave rise to a long-standing challenge to harness the adequacy of the dielectric continuum model for the magneto-bound polarons in CdTe which maintains the value $\alpha \sim 0.3$ of the coupling constant. But the experimental data on the Zeeman splitting in the $1s \to 2p$ shallow-donor-impurity transitions in CdTe at high magnetic fields obtained by Cohn *et al.*, (1972) have been precisely described in the framework of a second-order perturbation theory with band non-parabolicity taken into account using the value $\alpha = 0.286$ for the Fröhlich coupling constant following from Eq. (1c) (Shi *et al.*, 1995). It has been revealed in the latter work, that Cohn *et al.* (1972) had to use as a fitting parameter the value $\alpha = 0.4$ higher than the above-mentioned Fröhlich coupling constant, in order to compensate the underestimation of the polaron effects in the calculation of the transition energies.

1.4.2 Cyclotron resonance of polarons in 2D

Cyclotron resonance experiments have been performed on the 2DEG, e. g., in InSb inversion layers and in GaAs-Al$_x$Ga$_{1-x}$As heterostructures (Scholz *et al.*, 1983; Seidenbuch *et al.*, 1984; Sigg *et al.*, 1985; Merkt, 1985).

Several theoretical studies have been presented to analyse these experimental results for the 2DEG. In those works the cyclotron mass was obtained from the positions of the energy levels (Das Sarma, 1984; Larsen, 1984a,b; Peeters, Devreese, 1985; Peeters *et al.*, 1986b,c).

The theory of cyclotron resonance in the 2DEG, for cases where the electron-phonon interaction plays a significant role is reviewed by Devreese and Peeters (1987). Like in 3D (Peeters, Devreese, 1986) the theory is expressed in terms of the memory function formalism. In this treatment the magneto-optical absorption itself is calculated and the transition frequencies (rather than the individual energy levels) are obtained directly. Here the application was limited to the weak-coupling regime.

Some results of this work are:

- a) first the magneto-absorption spectrum was calculated, at weak coupling, for one polaron in 2D. A Landau-level broadening parameter is introduced phenomenologically in order to remove the divergencies in the magneto-optical absorption spectrum. The effect of the nonzero width of the 2DEG is incorporated along with nonparabolicity. The experimental data for p-InSb inversion layers can be adequately explained by this theory.

- b) To account for the cyclotron-mass data in GaAs-Al$_x$Ga$_{1-x}$As heterostructures it is essential to include many-body effects. Both the "occupation effect" (Pauli principle) and the effects of screening were included, on top of the effect included in the one-polaron studies under a).

It is also worth mentioning that, although for one electron the polaron effect is enhanced by the 2D-confinement, in reality e. g., in GaAs-Al$_x$Ga$_{1-x}$As with $n_e \geq 1.4 \times 10^{11}\ cm^{-2}$ screening helps to reduce the polaron effect in

2D so that it becomes smaller than its 3D counterpart. For sufficiently large densities the polaron mass in 2D is not a monotonically increasing function of ω_c but shows structure where the filling factor becomes an integer (Peeters *et al.*, 1988a,b).

It is obvious, both in the case of InSb and that of GaAs-Al$_x$Ga$_{1-x}$As that polaron effects do occur, even if these are weak-coupling materials.

A nice example, clearly demonstrating the polaron coupling is provided by the cyclotron resonance in a 2DEG which naturally occurs in InSe where $\alpha \approx 0.3$ (Nicholas *et al.*, 1992). One clearly sees, over a wide range of magnetic fields, the two distinct polaron branches separated by as much as $0.4\omega_{LO}$ at resonance (Fig. 5). Polaron cyclotron resonance has even been observed in n-type ZnS up to 220 T by Miura *et al.* (1994).

A quantitative interpretation of the cyclotron resonance measurements in n-GaAs and AlGaAs-GaAs heterojunctions was obtained on the grounds of the polaron theory with taking into account three factors: dimensionality, band nonparabolicity and screening (Sigg *et al.*, 1985). Impurity-bound resonant magnetopolarons have been clearly observed in bulk GaAs and GaAs-Al$_x$Ga$_{1-x}$As multiple quantum wells (Cheng *et al.*, 1993).

1.4.3 Formal developments

Also to treat Fröhlich polarons in a magnetic field the Feynman path integral proved to be a most powerful method extending the possibilities of perturbation theory and Hamiltonian variational calculations.

From the methodological point of view the introduction of the total angular momentum operator of the polaron

$$\hat{L}_z = \hat{l}_z + i\hbar \sum_{\mathbf{k},\mathbf{k}'} a^\dagger_{\mathbf{k}'} a_{\mathbf{k}} (k_x \frac{\partial}{\partial k_y} - k_y \frac{\partial}{\partial k_x}) \delta_{\mathbf{k},\mathbf{k}'} \quad (15)$$

(with $\hat{l}_z$ denoting the electron angular momentum) is useful for Hamiltonian treatments of polarons in a magnetic field (Evrard *et al.*, 1970). Later this operator was used in studies on excitons, An operator algebra method was developed by Larsen (1984), useful to study higher-order effects for polarons in magnetic fields, when expanding in powers of α.

1.5 The bound polaron

A polaron can be bound to a charged vacancy or to a charged interstitial. To a first approximation this system can be approximated by adding the Coulomb potential energy operator ($-e^2/\epsilon_\infty|\mathbf{r}| \equiv -\tilde{\beta}/|\mathbf{r}|$, $\mathbf{r}$ is the vector operator characterizing the electron position with respect to the center of the vacancy or of the interstitial) to the Fröhlich Hamiltonian.

Intuitively one expects that the weak-coupling polaron spectrum for the bound polaron is approximately given by a Bohr formula adapted to take into account the polaron mass:

$$E_n = -\alpha\hbar\omega_{LO} - \frac{m_b e^4}{2\hbar^2 n^2 \epsilon_0^2} - \frac{\alpha}{12}\frac{m_b e^4}{\hbar^2 n^2} + O(\alpha^2)\ (n = 1, 2, \ldots). \quad (16)$$

Expansions refining Eq. (16) were derived first using approximate schemes for perturbation theory (Bajaj, 1972); later a rigorous result for the binding energy E_n up to order α was obtained (Engineer, Tzoar, 1972).

Further schemes to treat the groundstate energy of the bound polaron (and approximations for some of the excited states) have been developed by Platzman (1962), Larsen (1969), Devreese *et al.* (1982), Adamowski (1985).

Brandt and Brown (1969) have interpreted some structure in their infrared optical absorption spectra of AgBr as caused by the bound polaron; in particular the 168 cm^{-1} absorption line has been analyzed as a transition between a 1s and a 2p state (modified by the polaron interaction). Also higher excited states and LO-phonon sidebands play a role in this spectrum [see e. g. (Bajaj, 1972)] (Fig. 6). The bound polaron is related to the F-center. In Tables 2 and 3 some energy levels of the bound polaron are tabulated.

2 The Small Polaron

2.1 The small-polaron concept. Role of localization

An electron or a hole trapped by its self-induced atomic (ionic) displacement field in a region of linear dimension ("radius"), which is of the order of the lattice constant, is called *small polaron* (Fröhlich, 1957; Sewell, 1958; Fröhlich, Sewell, 1959; Holstein, 1959; Emin, Holstein, 1976). An excellent survey of the small-polaron physics relevant to the conduction phenomena in non-crystalline materials and to the metal-insulator transitions has been given by Mott (1987, 1990). As distinct from large polarons, small polarons appear due to short-range forces. Thus, in certain materials, in particular in some oxydes, the induced lattice polarization is essentially localized in a volume of the order of a unit cell. Hence, the charge carrier is localized on an individual lattice site during a time which can become large compared to the *localization time* describing the relaxation of the lattice to the small-polaron state. The localization time is of the same order of magnitude as the period of a lattice vibration, ω_{LO}^{-1}.

Because for small polarons the lattice polarization is mostly confined to one unit cell, the atomicity of the solid is felt by the carrier; a complete treatment of small polarons should therefore start from an *ab initio* calculation which takes into account the detailed local structure of the solid; the

Fröhlich continuum approximation would not be adequate. Nevertheless, actual small-polaron theories as developed, e. g., by Yamashita and Kurosawa (1958), Holstein (1959) and others are based on analytical approximations as a starting point. Thus, the adiabatic eigenstates of an electron placed in a deformable continuum were shown to depend drastically on the character of the electron-lattice interaction as well as on the dimensionality of the system (Emin, Holstein, 1976). As distinct from the case of the long-range interaction with a stable large-polaron state, for the short-range interaction in a three-dimensional system there exist two stable states, namely, an unbound electron in an undeformed continuum and an electron collapsed in an infinitesimally localized self-induced potential well. The former is analogous to the band electron state in a rigid lattice, the latter models a small-polaron state. It is also worthwhile that the common action of a long-range and of a short-range forces was found to yield always a small-polaron-like state and — in a certain region of the interaction strengths — a large-polaron state. Thus, even from the early analysis a possibility of a *coexistence* of the both types of polarons can be distinctly deduced.

In the modern theories [see, e. g. (Alexandrov, Mott, 1994)], the small-polaron energy is regarded to consist of the following parts:

- a) the kinetic energy of the charge carrier in a rigid lattice which, as distinct from large polarons, is considered to originate from the intersite transfer due to tunneling;
- b) the energy of the atomic (ionic) displacements field, describing the lattice distortion;
- c) the potential energy of the charge carrier in the potential well formed by these displacements.

The interaction of the localized electron (hole) with the lattice vibrations then induces the charge carrier to jump from one atom (or ion) to a neighbouring one. This process is called *hopping*. The detailed physical picture of hopping (Lang, Firsov, 1962) suggests a sequence of the acts of small-polaron disintegration and reappearance as follows. At sufficiently high temperatures $k_BT > \hbar\omega_{LO}/4$, the typical time interval between jumps Δt satisfies the inequalities: $t_0 \ll \Delta t \ll t_p$, where $t_0 \sim \hbar/[(W_H k_B T)^{1/2}]$ (with W_H, the thermal activation energy for hopping) denotes the *jump-over* time and $t_p \sim \hbar/\Delta E_p$ (with ΔE_p, the small-polaron bandwidth) is the tunneling time. Hence, an electron remains most of the time at a site, suffering a hopping transition from site to site rather rarely, but on average earlier, than a tunneling occurs. As far as the jump-over time is much shorter than the period of a lattice vibration, $t_0 \ll \omega_{LO}^{-1}$, under a hopping transition the electron "jumps out of" the old potential well due to its self-induced lattice deformation, thus initiating a multiphonon process of the lattice relaxation: the small-polaron state disappears. But the time interval between jumps is much larger than the localization time, $\Delta t \gg \omega_{LO}^{-1}$. This inequality describes the *anti-adiabatic limit*: the atoms (ions) can adiabatically follow the motion of an electron, contrary to the case of a large polaron (see section 1.2.1). Thus, a new potential well due to the lattice deformation adapted to the new position of the electron is formed: a renascence of a small-polaron state occurs.

Also in the case of small polarons the relevant phonons are commonly the LO phonons. A simple estimate of the temperature dependence of mobility can be obtained starting from the following The larger the number of LO phonons n_{ph} present in the solid, the larger the mobility μ_{SP} of the small polaron:

$$\mu_{SP} \sim n_{ph}. \quad (17)$$

For sufficiently low temperatures $n_{ph} = e^{-\hbar\omega_{LO}/kT}$ and, as a consequence, we find

$$\mu_{SP} \sim e^{-\hbar\omega_{LO}/kT}. \quad (18)$$

It should be emphasized that the mobility of small polarons is therefore *thermally activated* and its temperature dependence is totally different from that of Fröhlich polarons [compare e. g. Eq. (18) with Eq. (10a)].

A more detailed theoretical treatment of the small-polaron mobility [see (Lang, Firsov, 1962; Reik, 1972)] leads to the following formula, valid for $T > \theta_D/2$ (θ_D is the Debye temperature of the crystal):

$$\mu_{SP} = \frac{ea^2\omega_{LO}}{6k_BT} \exp\left(-\frac{W_H}{k_BT}\right), \quad (19)$$

where a is the lattice constant of the crystal in which the small polaron occurs, W_H is the thermal activation energy for hopping and is given by 1/2 the small-polaron binding energy.

The Arrhenius-type activated behaviour of the form (19) of a mobility has been used as a fingerprint to identify small-polaron behaviour in solids. One of the earliest studies concerned one of the uranium oxydes UO_{2+x} (Devreese, 1963; Nagels *et al.*, 1964). Subsequently small polarons were invoked to interpret the conductivity in many oxydes (Mott, Davis, 1979), in particular in transition metal oxydes. It should be mentioned that often the measured quantity is the Hall-mobility rather than the drift mobility. The theory of the Hall mobility of small polarons due to hopping (Friedman, Holstein, 1963; Austin, Mott, 1969) leads to

$$\mu_{Hall} \propto T^{-\frac{1}{2}} \exp\left(-\frac{W_H}{3k_BT}\right). \quad (20)$$

The relation between Hall and drift mobility is not simple, and the Hall mobility depends, e. g., on the interference between several hopping processes [see a comprehensive review by Austin and Mott (1969)]. For s-carriers the Hall coefficient turns out to be always negative.

2.2 Standard small-polaron theory

As shown above, small polarons — at sufficiently high temperature — are characterized by diffusive motion and the band-picture with its Bloch states breaks down; in the low-temperature limit the band picture reappears in the theoretical description although experimental evidence for band conduction has been limited.

The fact that the Bloch-band picture breaks down is connected with the narrowing of the band gap which develops as the carrier becomes more and more localized, resulting in an increasing effective mass and, in the limit, in self-trapping. E. g. in KCl the material characteristics are such that a valence band hole gets self-trapped due to its polaron interaction with the lattice (Stoneham, 1979). The self-trapping of the hole is a subtle process, but the evidence is that it is related to the polaron formation in interplay with the Jahn-Teller effect (Stoneham, 1979).

For the quantitative treatment of small polarons the so-called molecular crystal model of Holstein (1959) is perhaps most illuminating. Without going into the mathematical details of this model, we mention its basic ingredients: a linear (1D) chain is considered with N diatomic molecules in which an excess electron is moving. With this model, the occurrence of two regimes, separated by a characteristic temperature typically of order 0.4 to $0.5\,\hbar\omega_{LO}/k_B$, is established theoretically: a) hopping induced by phonons and b) Bloch-type band motion. For hopping motion of small polarons, Holstein derived the following expression for the hopping mobility:

$$\mu = \frac{ea^2}{k_B T}\frac{J^2}{\hbar^2\omega_{LO}}\left[\frac{\pi}{\gamma\cosh\left(\frac{\hbar\omega_{LO}}{4k_B T}\right)}\right]^{\frac{1}{2}}\exp\left[-2\gamma\tan\left(\frac{\hbar\omega_{LO}}{4k_B T}\right)\right], \quad (21)$$

where J is a two-center overlap integral, γ is a measure for the electron-phonon coupling strength for small polarons to be distinguished from the large polaron coupling constant α ($2J$ corresponds to the width of the electronic Bloch band which is supposed to be relatively small in small-polaron theory).

An important role in small-polaron theory belongs to the distinction between adiabatic and non-adiabatic hopping transitions [roughly speaking, the adiabatic regime is characterized by the fact that the electron follows the atomic (ionic) motion instantaneously], see for the details the monograph by Klinger (1979).

The formation of small bipolarons by coupling of electrons to acoustic phonons and in disordered media was examined by Cohen *et al.* (1984). The study of small-polaron properties has been extended and studied in depth by Mott who identified and analyzed many instances of small-polaron transport including variable-range hopping, in which electrons hop over a range of distances and not only between nearest neighbours, and the role of small polarons in amorphous semiconductors (Mott, 1990). The coherence and dynamics of small polarons in the presence of disorder were represented in terms of two characteristic energies: the polaron bandwidth specifies the energy scale of disorder at which the polarons become localized as composite particles, while the bare electron bandwidth defines the energy scale at which the polaron ceases to be a composite particle (Spicci *et al.*, 1994).

In the theory of small polarons there are still some open fundamental questions which have been a subject of considerable recent investigation. Among the urgent issues: (i) the problem of the relevance of the Bloch-like states for a single small polaron in spite of the retardation, and (ii) the study of the nature and properties of quasiparticles in many-polaron systems, which are of especial interest for the polaron, bipolaron and hybrid polaron-bipolaron pictures of high-T_C superconductivity (see Sec. 5) should be pointed out.

2.3 Experimental evidence

Experimentally small-polaron effects have been analyzed, e. g., in KCl, LiF, NiO, MnO, TiO_2, $BaTiO_3$, $SrTiO_3$, $LaCoO_3$,... We refer to the reviews by Appel (1968) and Firsov (1975) for more details. More recently, de Jongh (1988), Micnas *et al.* (1990), Alexandrov and Krebs (1992) and Alexandrov and Mott (1994) surveyed in detail both the principles and the main results of the small-polaron theory in the context of the (bi)polaronic approach in the physics of high-T_C superconductors and tried to interpret some experimental data in different materials in terms of small polarons and small bipolarons.

The study of the optical absorption for small polarons is complex. A representative example is shown in Fig. 7, where the real part of the ac conductivity, describing the small-polaron absorption, as derived from the Kubo formula, is shown for various Γ ($\Gamma = \hbar/4\tau_0 k_B T$, where τ_0 is 1/4 times the "hopping time") (Reik, Heese, 1967). Note the completely different character of the optical absorption for small polarons as compared to large polarons.

In analyzing experimental transport data also thermoelectric power measurements are used; the theoretical study of the thermopower for small polarons has revealed that no polarization energy is transferred by the polaron motion.

Mobile polarons, observed in WO_{3-x} by Gehlig and Salje (1983), were shown to exhibit at 130 K a transition from a regime of hopping conductivity, characterized by a constant activation energy, to a regime of band conductivity, in which the process is not activated. With increasing carrier density, small polarons are formed up to a density, which is equal to the concentration of the sites at which they can be localized. At this critical density the dc electrical conductivity shows a phase transition, which these authors interpret as an Anderson-type transition: a change from a thermally activated small-polaron behaviour to a metallic temperature dependence occurs. the critical density was found to be about $3.7{\times}10^{21}$ cm^{-3} in WO_{3-x} (Salje, Güttler, 1984) and $1.7{\times}10^{21}$ cm^{-3} in $NbO_{2.5-x}$ (Rüscher *et al.*, 1988). At higher densities, two type of carriers are suggested to coexist: small polarons, on the one hand, and, on the other hand, conducting carriers which can be regarded as large polarons. The crossover from small-polaronic to metallic temperature dependence of the conductivity is consistently demonstrated by the Arrhenius plot for five different chemical compositions $NbO_{2.5-x}$. A thermally activated small-polaron conductivity seems to occur at lower degrees of reduction than that of $NbO_{2.49}$. This crossover scenario is strongly supported by the fact, that close to the same critical densities as mentioned above the saturation of the "integral intensity" of the polaronic absorption occurs, see Fig. 8.

Quite recently, the dc electrical conductivity of a slightly hyperstoichiometric sample of polycrystalline UO_{2+x} was interpreted (Casado *et al.*, 1994) in the framework of small-polaron theory, where some discrepancies between the semi-empirical values of the small-polaron self-energy and the thermal activation energy, from the one side, and those obtained as a result of a fully microscopic calculation, from the other side, are revealed.

The recent measurements of the Seebeck coefficient of $BaBi_{0.25}Pb_{0.75}O_{3-\delta}$ with an oxygen deficiency by Hashimoto *et al.* (1995) suggest the coexistence between the band charge carriers of high mobility, on the one side, and localized charge carriers of low mobility, on the other side (Fig. 9). Namely, in the low-temperature region, $T < 200$ K, the decrease of the (negative) Seebeck coefficient with T is supposed to be due to large electron polarons, while a temperature-activated behaviour of the (positive) Seebeck coefficient above room temperature is attributed by the authors to small hole polarons. A non-phenomenological interpretation of such experiments requires a theoretical approach which would combine the large- and the small-polaron concepts.

A complex of experimental results on dielectric relaxation, ac and dc conductivities of $La_{1-x}Sr_xFeO_3$ with $0.05 \le x \le 0.3$ obtained by Jung and Iguchi (1995) was self-consistently explained in terms of small polarons (see, e. g., Arrhenius plot for conductivity in Fig. 10).

3 Bipolarons and Polaronic Excitons

When two electrons (or two holes) interact with each other simultaneously through the Coulomb force and via the electron-phonon-electron interaction either two independent polarons can occur or a bound state of two polarons — the *bipolaron* — can arise (Vinetskii, 1961; Hiramoto, Toyozawa, 1985; Adamowski, 1989). Whether bipolarons originate or not, depends on the competition between the repulsive forces (direct Coulomb interaction) and the attractive forces (mediated through the electron-phonon interaction).

The bipolaron can be *free* and characterized by translational invariance, or it can be *localized*. According to Alexandrov and Ranninger (1981 a,b), the many-electron system on a lattice coupled with any bosonic field turns out to be a charged Bose-liquid, consisting of small bipolarons in the strong-coupling regime.

Similarly to the case of a bipolaron, an electron and a hole in a polarizable medium interacting with each other simultaneously both through the Coulomb force and via the electron-phonon-hole interaction, form a quasi-particle — the *polaronic exciton*.

3.1 Fröhlich bipolarons

In this section the case of free bipolarons for electrons or holes interacting with longitudinal optical phonons is discussed for the case of the continuum limit. They are referred to as Fröhlich bipolarons.

Fröhlich bipolarons are described by the following Hamiltonian

$$\begin{aligned} H &= \sum_{j=1,2}\left[\frac{\mathbf{p}_j^2}{2m_b}+\sum_{\mathbf{k}}(V_k a_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}_j}+V_k^* a_{\mathbf{k}}^\dagger e^{-i\mathbf{k}\cdot\mathbf{r}_j})\right] \\ &\quad +\sum_{\mathbf{k}}\hbar\omega_k a_{\mathbf{k}}^\dagger a_{\mathbf{k}}+U(\mathbf{r}_1-\mathbf{r}_2), \quad (22) \end{aligned}$$

where $\mathbf{p}_j, \mathbf{r}_j$ characterize the j'th electron (j=1,2), the potential energy for the Coulomb repulsion equals

$$U(\mathbf{r})=\frac{e^2}{\varepsilon_\infty|\mathbf{r}|}\equiv\frac{U}{|\mathbf{r}|}, \quad (23)$$

ε_∞ is the high-frequency dielectric constant and the other symbols in Eq. (22) are the same as those in Eq. (1a). Note that one always has

$$U>\sqrt{2}\alpha \quad (24)$$

($\hbar=\omega_{LO}=m_b=1$): this inequality expresses the obvious fact that $\varepsilon_0>\varepsilon_\infty$.

In the discussion of bipolarons often the ratio

$$\eta=\frac{\varepsilon_\infty}{\varepsilon_0} \quad (25)$$

of the electronic and static dielectric constant is used ($0\leq\eta\leq1$). It turns out that bipolaron formation is favoured by smaller η. To estimate the order of magnitude of the quantities involved one may express α and U as follows:

$$\alpha=\sqrt{\lambda}\left(\frac{1}{\varepsilon_\infty}-\frac{1}{\varepsilon_0}\right), \quad (26a)$$

$$U = \sqrt{2\lambda}\frac{1}{\varepsilon_\infty} \quad (26b)$$

with

$$\lambda = \frac{m_b}{m_e}\frac{R_y^*}{\hbar\omega_{LO}}. \quad (26c)$$

The effective Rydberg is characterized by the electron (hole) band mass m:

$$R_y^* = \frac{m_b e^4}{2\hbar^2}. \quad (27)$$

Verbist *et al.* (1990, 1991) analyzed the Fröhlich bipolaron using the Feynman path integral formalism. Quite analogously to the above discussed relations (12 a to d), a scaling relation was derived between the free energies F in two dimensions $F_{2D}(\alpha, U, \beta)$ and in three dimensions $F_{3D}(\alpha, U, \beta)$:

$$F_{2D}(\alpha, U, \beta) = \frac{2}{3}F_{3D}(\frac{3\pi}{4}\alpha, \frac{3\pi}{4}U, \beta). \quad (28)$$

This is the generalization to bipolarons of the scaling relation for a single Fröhlich polaron (Peeters, Devreese, 1987). Physically the scaling relation implies that bipolaron formation will be facilitated in 2D as compared to 3D. (The critical value for bipolaron formation α_c will be scaled with a factor $3\pi/4 \approx 2.36$ or: $\alpha_c^{(2D)} = \alpha_c^{(3D)}/2.36$).

Smondyrev *et al.* (1995) derived analytical strong-coupling asymptotic expansion in inverse powers of the electron-phonon coupling constant for the large bipolaron energy at $T = 0$

$$E_{3D}(\alpha, u) = \frac{2\alpha^2}{3\pi}A(u) - B(u) + O(\alpha^{-2}), \quad (29a)$$

where the coefficients are closed analytical functions of the ratio $u = U/\alpha$:

$$A(u) = 4 - 2\sqrt{2}u\left(1 + \frac{u^2}{128}\right)^{3/2} + \frac{5}{8}u^2 - \frac{u^4}{512} \quad (29b)$$

and for $B(u)$ see the above-cited paper. The scaling relation (28) allows to find the bipolaron energy in two dimensions as

$$E_{2D}(\alpha, u) = \frac{2}{3}E_{3D}(\frac{3\pi}{4}\alpha, u). \quad (30)$$

A "phase-diagram" for the polaron—bipolaron system was introduced by Verbist *et al.* (1990, 1991). It is based on the generalized trial action. This phase diagram is shown in Fig. 11 for the 3D-case. A Fröhlich coupling constant as high as 6.8 is needed to allow for bipolaron formation. No definite experimental evidence has been provided for the existence of materials with such high Fröhlich coupling constant. (One of the highest α's reported is for RbCl where $\alpha \approx 3.8$ and for CsI where $\alpha \approx 3.7$, see Table 1).

Materials with sufficiently large α for Fröhlich bipolaron formation in 3D might exist but careful analysis (involving e. g. the study of cyclotron resonance), like the one executed for AgBr, AgCl (Hodby *et al.*, 1987) is in order to confirm this. Presumably some modifications to the Fröhlich Hamiltonian are also necessary to describe such high coupling because of the more localized character of the carriers in this case which makes the continuum approximation less valid.

The confinement of the bipolaron in 2D facilitates bipolaron formation at smaller α. From Fig. 12 it is seen that bipolarons can now be stable for $\alpha \geq 2.9$, a domain of coupling constants which is definitely realized in several solids. Intuitive arguments suggesting that bipolarons are stabilized in going from 3D to 2D had been given before but the quantitative analysis based on the path integral was presented by Verbist *et al.* (1990, 1991).

The stability of bipolarons has also been examined with the use of operator techniques where the center of gravity motion of the bipolaron was approximately separated from the relative electron (hole) motion [see (Bassani *et al.*, 1991)]. The results by Bassani *et al.* (1991) and by Verbist *et al.* (1990, 1991) tend to confirm each other.

The bipolaron was also approached (Hiramoto, Toyozawa, 1985) in the path-integral representation using a special case of the trial action of (Verbist *et al.*, 1990; 1991); in this work the combined effect of LO phonons, acoustic phonons and deformation potential was analyzed.

Early work on bipolarons had been based on strong-coupling theory in which case the bipolaron stability can be expressed with η as the sole parameter. ($\eta < 0.08$ is a typical strong-coupling result for bipolaron stability.) It turns out that the numerical stability criteria (Verbist *et al.*, 1990) can be adequately formulated analytically for all α, for which the bipolaron is stable.

A very clear representation of experimental evidences for bipolarons, e. g. from the data on magnetization and electric conductivity in Ti_4O_7, as well as in $Na_{0.3}V_2O_5$ and polyacetylene, given by Mott (1990) is to be mentioned.

3.2 Polaronic excitons

Excitons constitute very interesting physical entities which in polarizable media are relevant to polarons: in polar systems they can be conceived as two interacting polarons of opposite charges (Haken, 1956; Toyozawa, 1963, 1964; Knox, 1963; Bassani, Baldereschi, 1973; Bassani, Pastori Parravicini, 1975; Adamowski *et al.*, 1981; Wallis, Balkanski, 1986).

The exciton groundstate energy in a polar crystal was determined by Pollman and Büttner (1975, 1977) taking into account the fact that the potential energy of the electron-hole interaction depends on the quantum state of the interacting particles due to the polaronic effect. Later on, many works were devoted to this problem. Similar considerations were applied by Petelenz and Smith (1981) to explain the dependence of the binding energy of an exciton-ionized donor complex on the electron-to-hole mass ratio in CdS and TlCl, and by Larsen (1981) to show that the ratio of the binding energy of the D^{-}-centers to that of neutral donors in AgBr and AgCl is as much as one order of magnitude larger than in nonpolar crystal. The binding enhancement is due to the *attraction* between the electrons and the static polarization charge induced by them in the central part of the ion. The experimental data on spectral photoconductivity in the systems Ca-Sr-Bi-Cu-O (Masumi *et al.*, 1988a) and Ba-Pb-Bi-O (Masumi *et al*, 1988b) have been interpreted to be due to an exciton-mediated bipolaronic mechanism. The recent experimental data on the reflectivity and its temperature dependence in La_2CuO_4 were interpreted in terms of polaronic excitons by Falk *et al.* (1992).

3.3 Localized bipolarons

Localized bipolarons tend to be *small* bipolarons, characterized by a radius of the order of the lattice constant.

For a small bipolaron, both constituting polarons can be localized either at the same lattice site [intrasite, or Anderson, bipolaron, see (Anderson, 1975)] or at two different lattice sites, e. g. at two neighbouring lattice sites (intersite bipolaron).

For two electrons (holes) on the same site the direct Coulomb repulsion is governed by the potential energy U. Whether or not two electrons remain at the same site, is determined by U_{eff}, the effective potential which arises if both the Coulomb repulsion and the electron (hole)-phonon or polaron interaction are taken into account. If the polaron interaction dominates ($U_{eff} < 0$) the Coulomb repulsion one speaks of *negative-U behaviour* and two carriers can be occupying the same site ("double occupancy of a lattice site"); a bipolaron localized on one site arises. Negative-U bipolarons have been suggested to occur e. g. in *chalcogenide glasses* (Anderson, 1975; Mott, 1990).

The intersite bipolaron can form *singlet* (bonding as well as anti-bonding) or *triplet* states (Fig. 13). Intersite singlet bipolarons are usually referred to as Heitler-London bipolarons, see for example (de Jongh, 1988).

Localization of bipolarons was investigated by many authors including Lannoo *et al.* (1959), Hubbard (1964), Stoneham and Bullough (1971), Anderson (1975), Mott (1990), to name a few. An extensive literature exists and a more complete discussion is given by Fisher *et al.* (1989). Localized bipolarons have been studied in numerous oxydes including Ti-oxydes, vanadium bronzes, $LiNbO_3$, WO_3.

Hybridization between coexisting localized bipolarons and itinerant electrons leads to a possibility of the coherent motion of bipolarons and their phase transition into a superfluid state upon lowering the temperature at a certain critical temperature (Ranninger, 1994), which seems to be relevant to the phenomena occurring in cuprates, bismuthates and fullerens.

4 Spin Polarons

Just like electrons or holes interact with the Bose-field of phonons, they can, because of the exchange interaction, interact with the magnon field. This gives rise to the formation of the *spin polaron* (or magnetic polaron). One of the first studies related to spin polarons is due to de Gennes (1960).

Intuitively one can imagine that e. g. in an antiferromagnet, the carrier spin polarizes the spins of the surrounding magnetic ions. The spin polaron consists of the carrier with its spin together with the lattice magnetization created by the carrier spin. Similar to the case of the dielectric polaron the physical properties of the carrier are influenced by the self induced magnetization cloud. The mechanism for the formation of spin polarons can be easily understood for materials with preference for antiferromagnetic alignment; the kinetic energy of a carrier can be reduced by reversing the spins of the surrounding ions; this allows the carrier to move more easily around these ions (Wood, 1991).

In principle spin polarons can arise in ferromagnets as well. Also the induced magnetic polarization can be characterized by ferromagnetic as well as antiferromagnetic alignment.

In general it is accepted that the evidence for the occurrence of *bound magnetic polarons* is more convincing than that for *free magnetic polarons* (Benoit á la Guillaume, 1993). Bound magnetic polarons occur when the carriers are localized (e. g. because they are bound to a donor or to an acceptor).

The bound magnetic polaron has been studied primarily in Mn-based semimagnetic semiconductors (SMSC). The bound magnetic polaron then originates from the exchange interaction between a rather localized unpaired carrier and the 5/2 spin of the surrounding Mn^{2+} ions. In the bound magnetic polaron ferromagnetic order occurs within the orbit of the bound carrier and the magnetic exchange leads to an increase of its binding energy. For spin polarons, e. g. in the case of EuS doped with GdSe (Mott, 1990), the basic interaction energy between a conduction electron spin and the surrounding magnetic moments is given by

$$J_{sf} s S |\Psi_s(0)|^2 V \quad (31)$$

J_{sf} is the energy of the ferromagnetic coupling between the spin s of the conduction electron and S the europium ion spin. $\Psi_s(0)$ is the wave function of the conduction electron at the origin. V is the atomic volume.

A transparent intuitive consideration due to Mott (1990) leads to a simple expression for the spin polaron radius:

$$R = \left(\frac{\hbar^2 \pi a^3}{4 m^* J_N} \right)^{1/5}, \quad (32)$$

where J_N is the energy, per moment, needed for a transition from the antiferromagnetic alignment to the ferromagnetic alignment, m^* is the effective mass of the carrier, a the lattice parameter of the host solid.

For the effective mass of the spin polaron the following expression has been derived (Mott, 1990):

$$m^*_{sp} = m^* e^{\gamma R/a} \quad (33)$$

with $\gamma \approx 1$.

5 Bipolarons and High-Temperature Superconductivity

Dielectric or Fröhlich bipolarons as well as spin bipolarons have been considered to possibly play a role in superconductivity. Also the "small-polaron" interaction was studied in the framework of superconductivity.

In fact already the charged bosons of Schafroth (1955) could be thought of as Fröhlich bipolarons. However although the London equation indeed results from a bipolaron gas model, a continuous behaviour of the specific heat C_V was found at the superconducting transition temperature in contradistinction from experiment. After the success of the BCS theory with its Cooper pairs consisting of electrons coupling in **k**-space: $|\uparrow, \mathbf{k}; \downarrow, -\mathbf{k}\rangle$, the bipolaron gas and the pairing in real space became a less central issue.

Nevertheless, theoretical models incorporating small bipolarons (localized Cooper pairs with electrons (holes) of opposite spin on nearest neighbour sites) and small bipolarons in narrow bands and characterized by hopping conductivity were still studied (Alexandrov, Ranninger, 1981a,b; Chakraverty *et al.*, 1987). These models had not predicted high-T_C superconductivity however.

After the discovery of high-T_C superconductivity alternative models (with respect to BCS) for superconductivity received renewed attention. It is experimentally clear that also in the high-T_C materials pairing of carriers takes place. However different coupling mechanisms might be at the basis of the pairing; e. g. coupling through acoustic plasmons has been considered.

In the present context a preliminary question is whether Fröhlich or spin bipolarons do form in high-T_C materials. This question has been investigated by Verbist *et al.* (1991) and the polaron-bipolaron phase diagram was applied e. g. to La_2CuO_4 (see Fig. 12). In this figure also $YBa_2Cu_3O_6$ is represented. On the basis of the existing experimental data it can be stated that the characteristic point in the polaron-bipolaron phase diagram for La_2CuO_4 and $YBa_2Cu_3O_6$ lies on the straight line through the origin and shown in the figure. Presumably the Fröhlich coupling is large enough in these materials that their α overlaps with the bipolaron existence region for α. It is remarkable that the existence line for bipolarons lies very close (La_2CuO_4) or penetrates ($YBa_2Cu_3O_6$) the very narrow existence domain for large bipolarons. It seems therefore *safe to assume* that Fröhlich bipolarons do occur in some of the high-T_C materials (Verbist *et al.*, 1990, 1994).

It should be re-iterated that the precise α-value characterizing the high-T_C materials is not known as long as the band mass has not been determined. It may also be observed that most other "polaron materials" (alkali halides etc.) find their characteristic points in the polaron-bipolaron phase diagram far away from the bipolaron stability area.

Cataudella *et al.* (1992), Iadonisi *et al.* (1995) have undertaken the study of the many-body physics of the bipolaron gas in an approximation comparable to that by Verbist *et al.* (1990), but based on a Hamiltonian formulation. Although the mathematics of this problem is complex and the studies are far from finalized, some promising features arise; especially the variation of T_C for the high-T_C materials as a function of the doping is well reproduced, be it with one fitting parameter.

On the basis of results by Verbist *et al.* (1991), also the optical spectra of bipolarons were analyzed; it was suggested that the mid IR-peak characterizing the high-T_C solids is related to relaxed excited states of the bipolaron.

Emin and Hillery (1989) studied the interplay between short- and long-range polaron interaction in the adiabatic (strong-coupling) approximation. This work joins the ideas of Schafroth and examines in more detail the character of the mobile charged bosons as bipolarons. (It should be noted that — in fact — the adiabatic theory does not lead to strong-coupling large Fröhlich bipolarons).

In discussing the bipolaronic superconductivity as a candidate theory for high-T_C superconductivity one should mention the analysis by Mott in terms of *spin bipolarons.* Mott (1991) has emphasized how a metal-insulator transition occurs in several of the high-temperature superconductors, the metal being superconducting. In analyzing this transition he suggests the formation of spin polarons and the possibility that they combine to form bipolarons. Those bipolarons could replace the Cooper pairs. Alexandrov *et al.* (1994) have also analyzed the non-degenerate gas of bosons above T_C. In particular, the linear T-behaviour of the resistivity, above T_C, was accounted for. Mott envisaged the possibility of two different mechanisms for superconductivity depending on the hole concentration (for one of the mechanisms, the bosons do not overlap, for the other they do) and stressed the analogy of high-T_C superconductors to the behaviour of superfluid ^{4}He. The quantitative formulation of this fact goes back to Alexandrov and Ranninger (1992) who used a mapping of the electronic specific heat of high-T_C superconductors onto that of ^{4}He to show that its λ-like temperature dependence may be described in terms of charged bosons.

Spin-bipolaron model has been invoked by Alexandrov *et al.* (1994b) to explain the experimental data on the Hall effect and resistivity in underdoped $YBa_2Cu_3O_{7-\delta}$ (Carrington *et al.*, 1993) basing on the assumption that at zero temperature a part of the spin bipolarons are in Anderson localized states due to disorder. The agreement between theory and experiment exists at least in the region of temperatures higher than the temperature T^* at which slope of resistivity changes. This is illustrated in Figs. 14 and 15, representing the temperature dependence of the Hall coefficient and of the resistivity for different values of the degree of reduction in $YBa_2Cu_3O_{7-\delta}$.

The Cooper pairing of small polarons has been regarded as a possible mechanism of high-T_C superconductivity — polaronic superconductivity, see e. g. a comprehensive review by Alexandrov and Mott (1994) and an extensive list of references therein. It was shown that there exists an intermediate region of the coupling constant, where the energy of interaction between small polarons (resulting from the interplay between the Coulomb repulsion and the attraction due to their interaction with the lattice) is smaller, or of the same order, as the small-polaron bandwidth, both being less or comparable to the phonon frequency. In this region, the BSC theory predicts superconductivity even for onsite repulsion, provided that it is weaker compared to the total intersite attraction of small polarons. It is the *polaronic narrowing* of the band which increases the estimated maximum value for the critical temperature when the interaction with high-frequency phonons is dominant. This maximum occurs for the intermediate value of the coupling constant which is situated at the boundary between the above-described polaronic superconductivity region, on the one hand, and the bipolaronic superconductivity region, on the other hand. The latter mechanism is considered to be relevant for the values of the coupling constant high enough to make the energy of attraction between small polarons much larger than the small-polaron bandwidth. In this case, the groundstate of the system of small polarons can be — in the first approximation — regarded as consisting of a phonon field and a set of immobile small *bipolarons*; the hopping term treated as a perturbation producing the bipolaronic motion.

A serious alternative to the picture developed by Alexandrov and Mott (1994) is the fermion-boson model considering a possibility of exchange between localized bipolarons and itinerant electrons which goes back to Ranninger and Robaszkiewicz (1985). Depending on the filling, this model gives either a BS-like state or a superfluid state of bipolarons with a dramatic increase of T_C beyond a critical concentration.

In summary of this section, it is realized that no definite theory for high-T_C superconductivity (whether or not it involves bipolarons) is available as yet; nevertheless dielectric bipolarons, spin-bipolaron gases and polaron-bipolaron mixtures seem to be systems of significant promise in attempting to construct such a theory.

6 Further Developments of the Polaron Concept

6.1 Polarons and bipolarons in polymers. Solitons

Many conjugated polymers (e. g., trans-polyacetylene) behave as quasi-1D semiconductors, where (the energy gaps are between 1.5 and 3.0 eV). The carrier transport in those systems seems to take place through *charged defects* originating as a result of doping. These charged defects are influenced by the polaronic interaction with the surroundings. At low temperature the transport is dominated by the motion of the defects; at higher doping levels hopping conductivity occurs. As is well known, the possible application of those polymers (including, e. g., those in aerospace technology) have attracted wide attention.

Su *et al.* (1980) have proposed a model Hamiltonian to study the physics of conjugated polymers. In analyzing the polaronic localized states related to the charged defects non-linear behaviour, characteristic of solitons, is revealed. The polaron-type excitations were experimentally observed in polyacetylene by Su and Schreiffer (1980).

Polarons in conjugated polymers constitute a challenging and vast subject; in the context of this article only its significance and main ingredients are pointed out; the reader is referred to comprehensive reviews by Yu (1988) and Fisher *et al.* (1989). Bipolarons might occur in polymers at higher dopant levels and the question of polaron-bipolaron conversion rates is a central one.

6.2 Modelling systems using the polaron concept

Originally the polaron was mainly studied to describe the electron-LO phonon interaction. The concept has been generalized to several systems where one or many fermions interact with a bath of bosons or to instances where such an approximation is meaningful. Table 4 lists several such cases. The fundamental concepts concerning a piezopolaron — it is a name for a quasi-particle arising due to piezoelectric interaction between an electron and acoustic phonons — were displayed by Mahan (1972) and Lax (1972). More recently, convincing experimental evidences on the significant role of piezopolarons in the of the electronic transport properties of CdS have been presented by Mahan (1990).

Other examples include the motion of a ^{3}He atom through superfluid helium (Bardeen *et al.*, 1969), or the dynamics of electrons (2DEG) at the surface of liquid He — "ripplonic polaron" (Jackson, Platzman, 1981; Devreese, Peeters, 1987).

Charges moving through liquids (many of which are characterized by polarizable atoms) have been modelled as "hydrated polarons" (Laria *et al.*, 1991). Even an electron interacting with plasmons ("plasmaron") was invoked to study the electron gas. A new subject concerns the occurrence of polarons in fullerenes (Matus *et al.*, 1992). Of special interest is the electronic polaron.

These extensions of the polaron concept are not treated in any detail here, but they illustrate the richness of the polaron concept.

A valuable extension of the polaron concept arises by considering the interaction between a carrier and the exciton field. One of the early formulations of this model was by Toyozawa (1963). The resulting quasiparticle is called the *electronic polaron*.

The self-energy of the electronic polaron (which is almost independent of wave number) must be taken into account when the bandgap of an insulator or semiconductor is calculated using pseudopotentials. E. g. if one calculates, with Hartree-Fock theory, the bandgap of an alkali halide, one is typically off by a factor of two. This was the original problem which was solved conceptually with the introduction of the electronic polaron (Toyozawa, 1963; Kunz, 1974). Also in the soft X-ray spectra of alkali halides exciton sidebands have been observed which seems to be due to the electronic polaron coupling (Devreese *et al.*, 1972).

The standard "Local Density Approximation" (LDA) does not provide the correct bandgap for semiconductors. The solution to this problem (Hybertsen, Louie, 1987; Godby *et al.*, 1988) via the so-called GW-approximation of Hedin (1965) is analogous in its basic interaction to Toyozawa's solution of the gap problem for strongly ionic crystals.

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Figure captions

Fig. 1. A conduction electron (or hole) together with its self-induced polarisation in a polar semiconductor or an ionic crystal forms a quasiparticle: a polaron.

Fig. 2. Internal excitations at strong coupling: E_0 — groundstate, E_1 — first relaxed excited state; E_{FC} — Franck-Condon state.

Fig. 3. Polaron mobility in AgBr (solid line) according to the low temperature self consistent approach of Kartheuser, Devreese and Evrard (1979) compared with the Hall data, from (Brown, 1981).

Fig. 4. Optical absorption Γ of polarons at $\alpha = 6$ as a function of frequency ν, expressed in units $\omega_{\rm LO}$, from (Devreese, 1972).

Fig. 5. The cyclotron resonance position plotted as a function of magnetic field for InSe from (Nicholas *et al.*, 1992).

Fig. 6. Induced absorption in AgBr at 9.3K from 150 to 320 cm^{-1}. The exciting light was in the region of the direct absorption edge. From (Brandt, Brown, 1969); reproduced by courtesy of the American Physical Society.

Fig. 7. Real part of the conductivity versus normalized frequency $\nu\tau$ for different values of the parameter Γ from (Reik, Heese, 1967); reproduced by courtesy of the Pergamon Press Ltd.

Fig. 8. Integral intensities of the polaronic absorption in dependence on the degree of reduction of $\mathrm{NbO}_{2.5-x}$ (●) and WO_{3-x} (□) from (Rüscher *et al.*, 1988); reproduced by courtesy of the Insitute of Physics Publishing.

Fig. 9. Seebeck coefficient of $\mathrm{BaBi}_{0.25}\mathrm{Pb}_{0.75}\mathrm{O}_{3.00}$: measured data (●) and phenomenoligical estimates (solid and dashed lines). From (Hashimoto *et al.*, 1995); reproduced by courtesy of the American Institute of Physics.

Fig. 10. Arrhenius plot for conductivity in $\mathrm{La}_{1-x}\mathrm{Sr}_x\mathrm{FeO}_3$ with $x = 0.05$ (●), $x = 0.10$ (○), $x = 0.20$ (solid boxes), $x = 0.25$ (□), $x = 0.30$ (◇) in comparison with small-polaron theory (solid lines). From (Jung, Iguchi, 1995); reproduced by courtesy of the Insitute of Physics Publishing.

Fig. 11. The stability region for bipolaron formation in 3D from (Verbist *et al.*, 1990). The dotted line $U = \sqrt{2}\alpha$ separates the physical region ($U \geq \sqrt{2}\alpha$) from the non-physical ($U \leq \sqrt{2}\alpha$). The stability region lies below the full curve. The shaded area is the stability region in physical space. The dashed line is determined by $U = \sqrt{2}\alpha/(1 - \varepsilon_\infty/\varepsilon_0)$ where we took the experimental values $\varepsilon_\infty = 4$ and $\varepsilon_0 = 50$. The critical point $\alpha_c = 6.8$ is represented as a full dot.

Fig. 12. The same as Fig. 11, but now for 2D, where the critical point is $\alpha_c = 2.9$. From (Verbist *et al.*, 1990).

Fig. 13. States of a model two-site, two-electron system where the electrons are coupled to the inter-atomic coordinate from (Fisher *et al.*, 1989); reproduced by courtesy of the Insitute of Physics Publishing.

Fig. 14. Hall coefficient of $YBa_2Cu_3O_{7-\delta}$ for various degrees of reduction: $\delta = 0.05$ ($\triangle$), 0.19 ($\bullet$), 0.23 ($\diamond$), 0.39 ($\circ$) (Carrington *et al.*, 1993) in comparison with theory. From (Alexandrov *et al.*, 1994b); reproduced by courtesy of the Elsevier Science Publishers.

Fig. 15. Resistivity of $YBa_2Cu_3O_{7-\delta}$ for various degrees of reduction in the same denotations as in Fig. 14 (Carrington *et al.*, 1993) in comparison with theory. T^* stands for the temperature at which the change in the slope of resistivity occurs. From (Alexandrov *et al.*, 1994b); reproduced by courtesy of the Elsevier Science Publishers.

Table 1: *Fröhlich coupling constants*

Material	α	Material	α
CdTe	0.31	KI	2.5
CdS	0.52	RbCl	3.81
ZnSe	0.43	RbI	3.16
AgBr	1.6	CsI	3.67
AgCl	1.8	TlBr	2.55
CdF_2	3.2	GaAS	0.068
InSb	0.02	GaP	0.201
KCl	3.5	InAs	0.052
KBr	3.05	$SrTiO_3$	4.5

Table 2: *Groundstate energy (in units* $\hbar\omega_{\mathrm{LO}}$*) of the bound polaron for several values of* α *and* $\tilde{\beta}$ *as obtained by Devreese et al. (1982) compared to the variational results by Larsen (1969)*

α	$\tilde{\beta} = 6.32$		$\tilde{\beta} = 4.47$	
	E (Devreese *et al.*, 1982)	E (Larsen, 1969)	E (Devreese *et al.*, 1982)	E (Larsen, 1969)
2	−14.66	−14.69	−8.60	−8.64
5	−23.0	−23.0	−15.21	−15.30
7	−29.41	−29.47	−20.52	−20.62
11	−44.6	−44.6	−33.4	−33.4

Table 3: *Calculated energy of the first excited 2p state (in units $\hbar\omega_{\mathrm{LO}}$) of the bound polaron for several values of α and $\tilde{\beta}$ as obtained by Devreese et al. (1982)*

	$\mathrm{E}_{2\mathrm{p}}$		
α	$\tilde{\beta} = 0$	$\tilde{\beta} = 1$	$\tilde{\beta} = 2$
1	-0.7626	-0.8775	-1.113
3	-1.971	-2.237	-2.628
5	-3.207	-3.644	-4.205
7	-4.600	-5.214	-5.955
9	-6.199	-6.996	-7.922
11	-8.029	-9.014	-10.13

Table 4: *Extensions of the polaron concept*

Concept	"Candidates"
Acoustic polaron	Hole in AgCl
Piezoelectric polaron	ZnO, ZnS, CdS
Electronic polaron	Bandstructure of all semiconductors
Spin polaron	Magnetic semiconductors
Bipolarons:	
One center	Amorphous chalcogenides
Two center	Ti_4O_7, vanadium-bronzes
Small polarons and hopping	Transition metal oxydes Polyacetylenes
Superconductivity and (bi)-polarons ("Localized electron pairs")	$BaPb_{1-x}$ (1981) Bi_xO_3 $LiTi_2O_4$ (1985) "High-T_C superconductivity"