POLARONS

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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. Cyclotron resonance, and therefore the behavior 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, its effective mass, and 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:

$$H = \frac{p^2}{2m_b} + \sum_k \hbar\omega_{LO} a_k^\dagger a_k + \sum_k (V_k a_k e^{i\mathbf{k}\cdot\mathbf{r}} + H.c.), \tag{1a}$$

where $\mathbf{r}$ is the position coordinate operator of the electron with band mass m_b, $\mathbf{p}$ is its canonically conjugate momentum operator, and $a_k^\dagger$ and a_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:

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

$$\alpha = \frac{e^2}{\hbar c}\sqrt{\frac{m_b c^2}{2\hbar\omega_{LO}}}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right). \tag{1c}$$

Here 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

1. the spatial extension of the polaron is large compared with the lattice parameters of the solid ("continuum" approximation);
2. spin and relativistic effects can be neglected;
3. the band electron has parabolic dispersion; and
4. 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

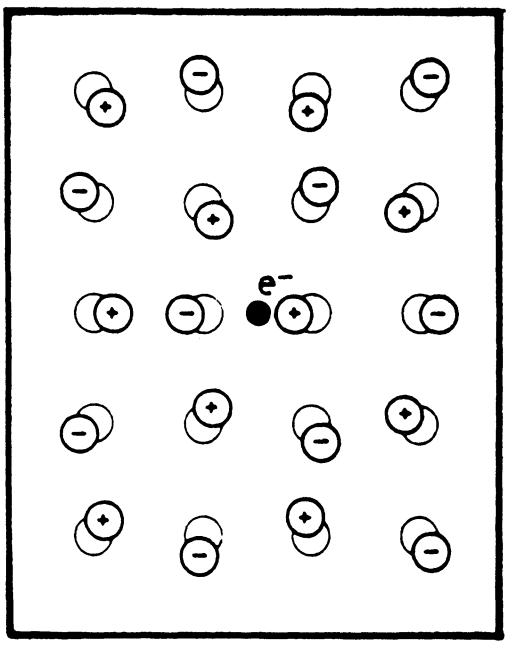

FIG. 1. A conduction electron (or hole) together with its self-induced polarization in a polar semiconductor or an ionic crystal forms a quasiparticle: a polaron.

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	1.53	CsI	3.67
AgCl	1.84	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

not appropriate insofar 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 Sec. 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 realizations of the polaron concept (small polarons, spin polarons, etc.) are discussed in later sections. For reviews on polarons, see Kuper and Whitfield (1963), Appel (1968), Devreese (1972), and 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,

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

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 that 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), and 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

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

where

$$\rho_{\mathbf{k}} = e\langle\Psi(\mathbf{r})|e^{i\mathbf{k}\cdot\mathbf{r}}|\Psi(\mathbf{r})\rangle, \tag{2c}$$

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 ground-state energy of the polaron E_0 (calculated with the energy of the uncoupled electron–phonon system as zero energy) takes the form

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

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

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

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 (RES) results (Pekar, 1951). Its energy is (Evrard, 1965; Devreese and Evrard, 1966)

$$E_{\text{RES}} = -0.041\alpha^2\hbar\omega_{\text{LO}}. \tag{3c}$$

In fact, both the FC state and the RES lie in the continuum* and, strictly speaking, are resonances (Fig. 2).

The strong-coupling mass of the polaron,

*The RES lies in the continuum of so-called scattering states, not indicated in Fig. 2.

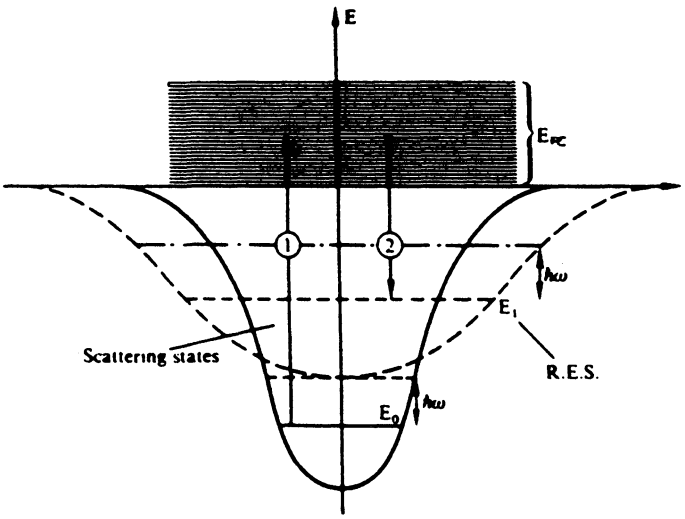

FIG. 2. Internal excitations at strong coupling: E_0, ground state; E_1, first relaxed excited state; E_{FC}, Franck–Condon state.

resulting again from the approximation (2), is given as

$$m^*/m_b = 1 + 0.0200\alpha^4. \tag{3d}$$

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

$$E_0/\hbar\omega_{LO} = -0.108\,513\alpha^2 - 2.836, \tag{4a}$$

$$m^*/m_b = 1 + 0.022\,7019\alpha^4. \tag{4b}$$

The main significance of the strong-coupling theory is that it allows a test of "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:

$$E_0 = -\alpha\hbar\omega_{LO} \tag{5a}$$

and

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

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

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

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:

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

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 that describes the polarization.

The LLP 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 LLP 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:

$$E_0/\hbar\omega_{LO} = -\alpha - 0.0123\alpha^2 - 0.00064\alpha^3 - \cdots (\alpha \to 0), \tag{7a}$$

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

Since then a lot of theoretical work has been devoted to obtaining 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: $2\ln(\sqrt{2}+1) - \frac{3}{2}\ln 2 - \frac{1}{2}\sqrt{2} \approx -0.015\,919\,62$ and $\frac{4}{3}\ln(\sqrt{2}+1) - \frac{2}{3}\ln 2 - 5\sqrt{2}/8 + \frac{7}{36} \approx 0.023\,627\,63$, respectively. At present, the following most accurate higher-order weak-coupling expansions are known: for the energy (Smondyrev, 1986; Selyugin and Smondyrev, 1989),

$$E_0/\hbar\omega_{\mathrm{LO}} = -\alpha - 0.015\,919\,6220\alpha^2 - 0.000\,806\,070\,048\alpha^3 - \cdots, \tag{7c}$$

and for the polaron mass (Röseler, 1968),

$$m^*/m_b = 1 + \tfrac{1}{6}\alpha + 0.023\,627\,63\alpha^2 + \cdots, \tag{7d}$$

which are a striking illustration of the heuristical value of Feynman's path-integral approach in the polaron theory as follows from comparison of Eqs. (7a) and (7b) with Eqs. (7c) and (7d), respectively.

1.2.3 All-Coupling Theory. Feynman Path Integral In the early 1950s, 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 QED ... (resulting in) ... a sum over all trajectories...." The resulting path integral is of the form (Feynman, 1955)

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

where $\beta = 1/k_{\mathrm{B}}T$. This path integral (8) has a great intuitive appeal: It shows the polaron problem as an equivalent one-particle problem in which the interaction, nonlocal 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 nonlocal in time) to simulate Eq. (8). It may be noted that the elimination of the phonon field (or the boson field in general) introduced through Eq. (8) 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 quite accurate limits. Feynman obtained the smooth interpolation between weak and strong coupling (for the ground-state energy). It is worth while 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

$$\frac{E_0}{\hbar\omega_{\mathrm{LO}}} \equiv \frac{E_{3\mathrm{D}}(\alpha)}{\hbar\omega_{\mathrm{LO}}} = -0.106\alpha^2 - 2.83 - \cdots \ (\alpha \to \infty), \tag{9a}$$

and for the polaron mass

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

Over the years, the Feynman model for the polaron has remained in many respects the most successful approach to this problem. Only recently an equivalent Hamiltonian formulation of this path-integral approach has been realized ($\omega_c = 0$) by Devreese and Brosens (1992). [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:

$$\mu \sim \exp(\hbar\omega_{LO}/k_B T). \tag{10a}$$

The first to point out the typical behavior (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

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

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

Feynman *et al.* (1962) (usually referred to as FHIP) 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:

$$\mu \equiv \mu_{3D}(\alpha) = \frac{e}{2m^*\omega_{LO}\alpha} \frac{3}{2}\left(\frac{w}{v}\right)^3 \times \exp\left(\frac{v^2 - w^2}{w^2 v}\right) \exp\left(\frac{\hbar\omega_{LO}}{k_B T}\right) \frac{k_B T}{\hbar\omega_{LO}}, \tag{10c}$$

where w and v are functions of α (also adequate for large α) deriving from the Feynman polaron model.* 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 explanation of 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 Frölich polarons, written from a unified point of view, was presented by Peeters and Devreese (1984).

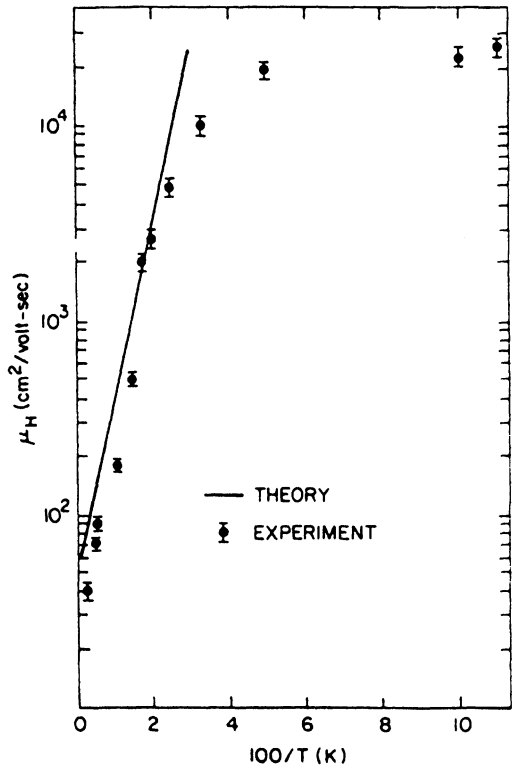

FIG. 3. Polaron mobility in AgBr (solid line) according to the low-temperature self-consistent approach of Devreese and co-workers (Kartheuser *et al.*, 1979) compared with the Hall data, from Brown (1981).

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

It was shown by the author and his coauthors (see Devreese, 1972) how the optical absorption of Fröhlich polarons, for all coupling, can be calculated starting from the FHIP scheme (which gives a derivation for the impedance function). This work led to the following expression for the optical absorption:

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

where ν is the frequency of the incident radiation and $\Sigma(\nu)$ is the so-called "memory function" that 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 Eq. (10d), in Devreese (1972) the three different kinds of polaron excitations, studied before only in asymptotic limits, are seen to appear in the spectra:

1. scattering states where, e.g., one real phonon is excited (the structure starting at $\nu = 1$);
2. RES; and
3. FC states.

2 and **3** can be seen in the works of the author and co-workers [Kartheuser *et al.*, 1969 (KED); Devreese and Evrard, 1966; Evrard, 1965]. Experimentally only the "scattering states" have been observed for free polarons (Finkenrath *et al.*, 1969); the RES play a role for bipolarons (Devreese *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 (Peeters and Devreese, 1986).

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 Devreese and collaborators (KED).

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

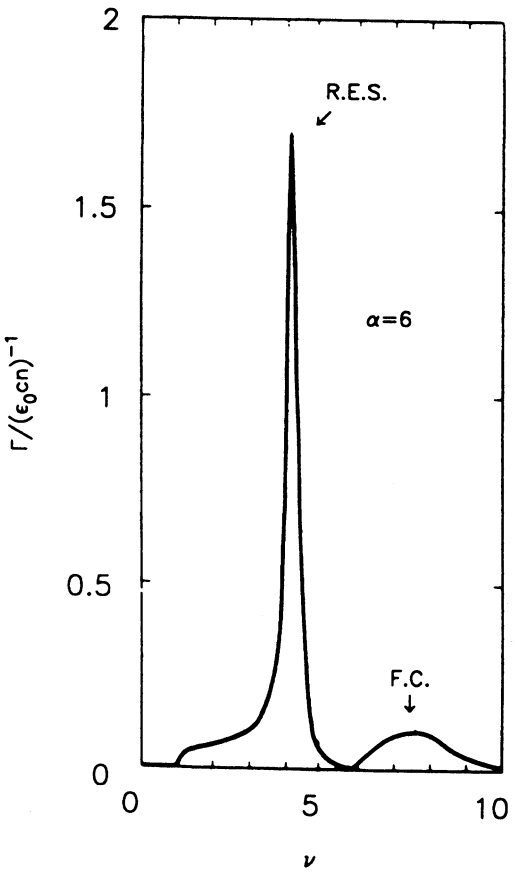

FIG. 4. Optical absorption Γ of polarons at $\alpha = 6$ as a function of frequency ν, expressed in units ω_{LO}, from Devreese (1972).

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 di-

mensions, 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):

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

valid because 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-energies $\Delta E/\hbar\omega_{LO}$ for a polaron in 2D for $\alpha \to 0$ and $\alpha \to \infty$ were derived by Devreese and co-authors (Xiaoguang *et al.*, 1985, XPD) and Das Sarma and Mason (1985):

$$\frac{\Delta E}{\hbar\omega_{LO}} \equiv \frac{E_{2D}(\alpha)}{\hbar\omega_{LO}} = -\frac{\pi}{2}\alpha - 0.063\,97\alpha^2 + O(\alpha^3) \quad (\alpha \to 0), \tag{11a}$$

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

The corresponding results for the polaron mass in 2D are (XPD)

$$\frac{m^*}{m_b} \equiv \frac{m^*_{2D}(\alpha)}{m_{2D}} = \frac{\pi}{8}\alpha + 0.127\,2348\alpha^2 + O(\alpha^3) \quad (\alpha \to 0), \tag{11c}$$

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

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:

$$E_{2D}(\alpha) = \tfrac{2}{3}E_{3D}(3\pi\alpha/4), \tag{12a}$$

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

$$Z_{2D}(\alpha,\nu) = Z_{3D}(3\pi\alpha/4),\nu), \tag{12c}$$

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

$$\mu_{2D}(\alpha) = \mu_{3D}(3\pi\alpha/4). \tag{12d}$$

Except for the investigations on polarons at the surface of liquid He (Jackson and Platzman, 1981; 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 and 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.* (1963), 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 and Larsen, 1966) and CdTe (Waldman *et al.*, 1969) provided first indications for these level-crossing and pinning phenomena. Detailed line-shape studies for weak coupling

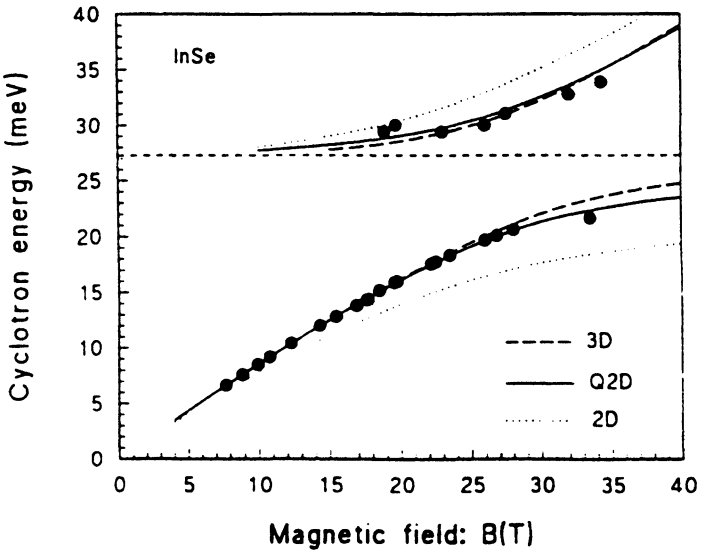

FIG. 5. The cyclotron-resonance position plotted as a function of magnetic field for InSe, from Nicholas *et al.* (1992).

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 Devreese and his co-workers (see Van Royen *et al.*, 1977).

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 $\beta = 1/k_B T$. The starting point is the expression of the free energy of the polaron as a path integral,

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

The "electron" contribution to the action S is

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

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 and Devreese, 1982) to simulate the polaron (retarded Coulomb) interaction and, in analogy to the zero–magnetic-field case, the Jensen–Feynman inequality was assumed to be valid:

$$F \le F_{\text{ph}} + F_m - \frac{1}{\beta} \langle S - S_m \rangle_m. \tag{13c}$$

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

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

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

A question of considerable significance has been 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 and Hibbs, 1965). Several works have been devoted to this challenging problem; see Brosens and Devreese (1988), Sec. 3.4 in Fomin and Pokatilov (1988), and Larsen (1991) for detailed reviews. Larsen (1985) revealed that

the ground-state levels of a 2D polaron obtained "variationally" on the basis of Eq. (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 ground-state level as the exact one, Larsen came to the conclusion that it would seem difficult to attach any particular sense to the variational ground-state level. However, it was pointed out that the adiabatic strong-coupling theory does not provide a rigorous asymptotic limit of high magnetic fields; see discussion in Devreese and Brosens (1991). It is also worth while to note that the perturbation ground-state energy can, however, itself be treated in some cases (see Fomin and 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 so far it has not been conclusively established that a choice of the parameters in the trial action made in Peeters and 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 and Platzman, 1962; Marshall and Chawla, 1970; Evrard *et al.*, 1970; Lépine and Matz, 1976) are obtained as special cases of the results by Peeters and Devreese (1982) who simply accepted the inequality (13c) as a working hypothesis. A prediction by Peeters and Devreese (1982) is that some quantities characterizing the internal structure of the polaron [called, e.g., $(\nu_\perp/\omega_\perp)^2$ 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 was therefore 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 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 that 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 used 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

$$\lim_{\epsilon \to 0} \frac{1}{\nu - \omega_c - \Sigma(\nu + i\epsilon)}, \tag{14a}$$

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

$$\langle e^{i\mathbf{k}\cdot\mathbf{r}(t)} e^{-i\mathbf{k}\cdot\mathbf{r}(0)} \rangle, \tag{14b}$$

where $\langle \cdot \rangle$ can be expressed as a path integral. $\Sigma(\nu + i\epsilon)$ is an intricate function that 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 formulation 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) based on the theory of magnetoabsorption by Peeters and Devreese (1986) provides a confirmation of the Fröhlich description of the polaron in a case where weak-coupling approximations are not adequate.

An interesting case is provided by the cyclotron-resonance data for CdTe (Johnson and 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 a 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 about 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 it turns out that the experimental data on the Zeeman splitting in the $1s \rightarrow 2p$ shallow-donor–impurity transitions in CdTe at high magnetic fields obtained by Cohn *et al.* (1972) can be precisely described in the framework of a second-order perturbation theory with band nonparabolicity 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 for 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_xGa_{1-x}As heterostructures (Scholz *et al.*, 1983; Seidenbusch *et al.*, 1984; Sigg *et al.*, 1985; Merkt, 1985; Hopkins *et al.*, 1989). Several theoretical studies have been presented to analyze 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 and 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 and 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.

Some results of this work are the following:

1. 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 divergences 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.
2. To account for the cyclotron-mass data in GaAs–Al_xGa_{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 **1**.

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–$Al_xGa_{1-x}As$ 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, Peeters *et al.* (1988a,b) revealed that the polaron mass in 2D is not a monotonically increasing function of ω_c but shows structure where the filling factor becomes an integer.

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

A nice example, clearly demonstrating the polaron coupling, is provided using the memory-function approach by the author and his colleagues (Peeters and Devreese, 1985, 1986c; Devreese and Peeters, 1986) through the analysis of the cyclotron resonance in a 2DEG that 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 by Peeters *et al.* (1988a,b) on the grounds of the polaron theory with three factors taken into account: dimensionality, band nonparabolicity, and screening. Impurity-bound resonant magnetopolarons have been clearly observed in bulk GaAs and GaAs–$Al_xGa_{1-x}As$ 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,

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

(with $\hat{l}_z$ denoting the electron angular momentum), is useful for Hamiltonian treatments of polarons in a magnetic field performed by Evrard *et al.* (1970). Later this operator was used in studies on excitons.

An operator-algebra method was developed by Larsen (1984a), 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 $(-e^2/\epsilon_\infty|\mathbf{r}| \equiv -\tilde{\beta}/|\mathbf{r}|$, where $\mathbf{r}$ 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:

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

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 and Tzoar, 1972).

Further schemes to treat the ground-state 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), and 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.

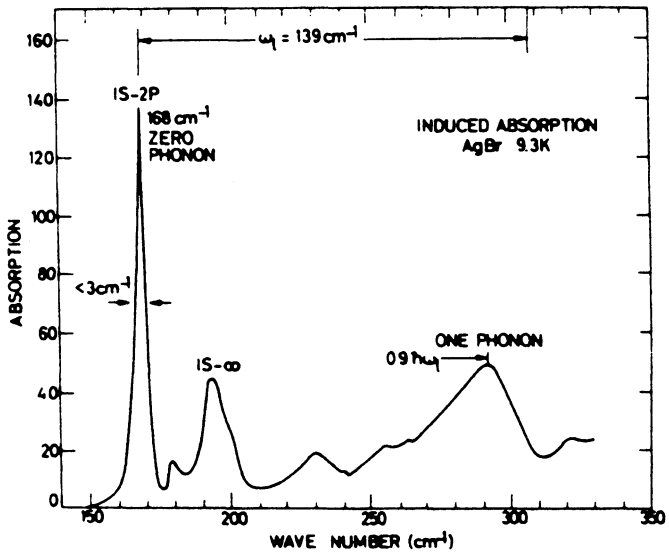

FIG. 6. Induced absorption in AgBr at 9.3 K from 150 to 320 cm^{-1}. The exciting light was in the region of the direct-absorption edge. From Brandt and Brown (1969), reproduced by courtesy of The American Physical Society.

Table 2. Upper bounds for the ground-state energy (in units $\hbar\omega_{LO}$) of the bound polaron for several values of α and $\tilde{\beta}$ as obtained by Devreese *et al.* (1982) compared with the results by Larsen (1969).

	$\tilde{\beta} = 6.32$		$\tilde{\beta} = 4.47$	
α	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

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") that is of the order of the lattice constant is called a *small polaron* (Fröhlich, 1957; Sewell, 1958; Fröhlich and Sewell, 1959; Holstein, 1959; Emin and Holstein, 1976). An excellent survey of the small-polaron physics relevant to conduction phenomena in non-crystalline materials and to metal–insulator transitions has been given by Mott (1987, 1990). As distinct from large polarons, small polarons appear as a result of overall short-range forces. Thus, in certain materials, in particular in some oxides, 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 that can become large compared with 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 car-

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

	E_{2p}		
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

rier; a complete treatment of small polarons should therefore start from an *ab initio* calculation that 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 and 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 worth while noting that the common action of a long-range and of a short-range force 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 the possibility of *coexistence* of both types of polarons can be distinctly deduced.

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

1. 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;
2. the energy of the atomic (ionic) displacements field, describing the lattice distortion; and
3. 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 neighboring one. This process is called *hopping*. The detailed physical picture of hopping (Lang and Firsov, 1962) suggests a sequence of the acts of small-polaron disintegration and reappearance as follows. At sufficiently high temperatures $k_B T > \hbar\omega_{LO}/4$, 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, undergoing a hopping transition from site to site rather rarely, but on average earlier than a tunneling occurs. If 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 due to 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, in contrast with the case of a large polaron (see Sec. 1.2.1). Thus, a new potential well due to the lattice deformation adapted to the new position of the electron is formed. A small-polaron state reappears.

Also in the case of small polarons the relevant phonons are commonly the LO phonons. A simple estimate of the temperature dependence of the 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:

$$\mu_{SP} \sim n_{ph}. \tag{17}$$

For sufficiently low temperatures $n_{ph} = \exp(\hbar\omega_{LO}/k_B T)$ and, as a consequence, we find

$$\mu_{SP} \sim \exp(\hbar\omega_{LO}/k_B T). \tag{18}$$

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 and Firsov, 1962; Reik, 1972) leads to the following formula, valid for $T > \theta_D/2$ (θ_D is the De-

bye temperature of the crystal):

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

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 $\frac{1}{2}$ the small-polaron binding energy.

The Arrhenius-type activated behavior of the form (19) of the mobility has been used as a fingerprint to identify small-polaron behavior in solids. The earliest studies concerned one of the uranium oxides, UO_{2+x} (Devreese, 1963; Nagels *et al.*, 1964). Subsequently, small polarons were invoked to interpret the conductivity in many oxides (Mott and Davis, 1979), in particular in transition-metal oxides. 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 and Holstein, 1963; Austin and Mott, 1969) leads to

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

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 that develops as the carrier becomes more and more localized, resulting in an increasing effective mass and, in the limit, in self-trapping. For example, in KCl the material characteristics are such that a valence-band hole gets self-trapped because of 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 the hopping motion of small polarons, Holstein derived the following expression for the mobility:

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

where J is a two-center overlap integral and 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 nonadiabatic 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 (1990), 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 neigh-

bors. He revealed the role of small polarons in amorphous semiconductors. 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 that have been a subject of considerable recent investigation. Among the urgent issues, we note

1. the problem of the relevance of the Bloch-like states for a single small polaron in spite of the retardation, and
2. 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).

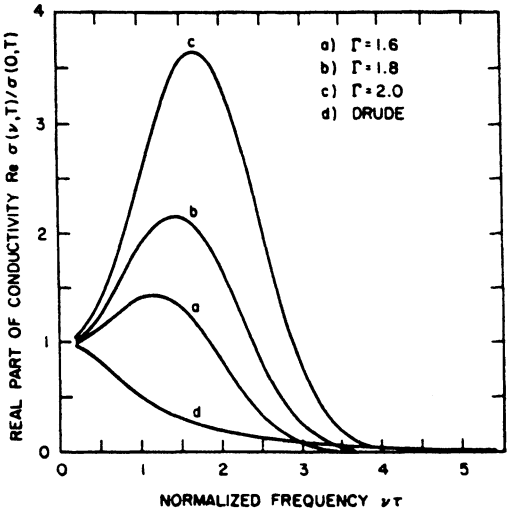

FIG. 7. Real part of the conductivity vs normalized frequency $\nu\tau$ for different values of the parameter Γ; from Reik and Heese (1967), reproduced by courtesy of Pergamon Press Ltd.

2.3 Experimental Evidence

Experimentally small-polaron effects have been analyzed, e.g., in UO_{2+x}, KCl, LiF, NiO, MnO, TiO_2, $BaTiO_3$, $SrTiO_3$, $LaCoO_3$, etc. 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 $\frac{1}{4}$ times the "hopping time") (Reik and Heese, 1967). Note the completely different character of the optical absorption for small polarons as compared with large polarons (see Fig. 4).

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 that 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 behavior to a metallic temperature dependence occurs. The critical density was found to be about 3.7×10^{21} cm^{-3} in WO_{3-x} (Salje and Güttler, 1984) and 1.7×10^{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 that can be regarded as

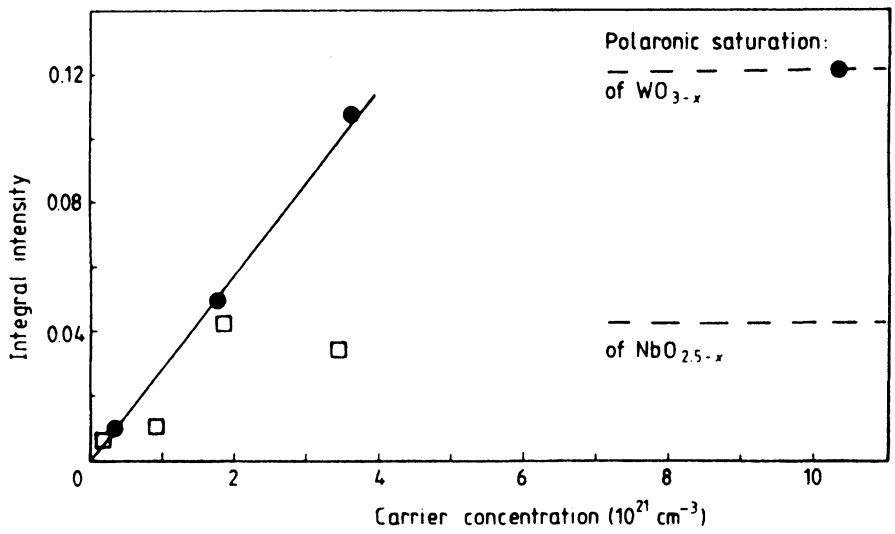

FIG. 8. Integral intensities of the polaronic absorption in dependence on the degree of reduction of $NbO_{2.5-x}$ (●) and WO_{3-x} (□); from Rüscher *et al.* (1988), reproduced by courtesy of Institute of Physics Publishing.

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, a 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 semiempirical 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 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 behavior of the (positive) Seebeck coefficient above room temperature is attributed by the authors to small-hole polarons. A nonphenomenological interpretation of such experi-

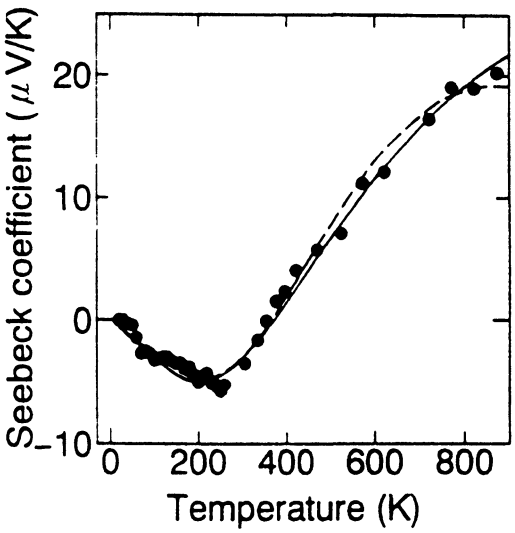

FIG. 9. Seebeck coefficient of $BaBi_{0.25}Pb_{0.75}O_{3.00}$: measured data (●) and phenomenological estimates (solid and dashed lines); from Hashimoto *et al.*, 1995, reproduced by courtesy of The American Physical Society.

ments requires a theoretical approach that would combine the large- and the small-polaron concepts.

A complex of experimental results on dielectric relaxation and ac and dc conductivities of $La_{1-x}Sr_xFeO_3$ with $0.05 \leq x \leq 0.3$ obtained by Jung and Iguchi (1995) was self-consistently explained in terms of small polarons (see, e.g., the 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* (Pekar, 1951)—can arise (Vinetskii, 1961; Hiramoto and 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).

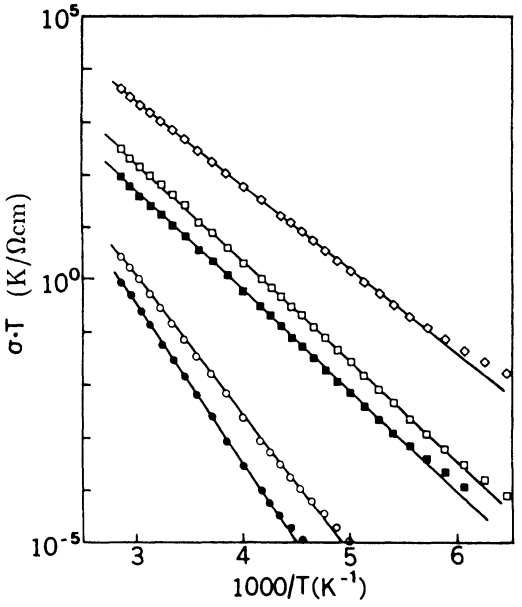

FIG. 10. Arrhenius plot for conductivity in $La_{1-x}Sr_xFeO_3$ with $x = 0.05$ (●), $x = 0.10$ (○), $x = 0.20$ (solid boxes), $x = 0.25$ (□), $x = 0.30$ (◇) in comparison with small-polaron theory (solid lines); from Jung and Iguchi (1995), reproduced by courtesy of Institute of Physics Publishing.

The bipolaron can be *free* and characterized by translational invariance, or it can be *localized.* According to Alexandrov and Ranninger (1981a,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 quasiparticle—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:

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

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

$$U(\mathbf{r}) = e^2/\epsilon_\infty|\mathbf{r}| \equiv U/|\mathbf{r}|, \tag{23}$$

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

$$U > \sqrt{2}\alpha \tag{24}$$

($\hbar = \omega_{\mathrm{LO}} = m_b = 1$): This inequality expresses the obvious fact that $\epsilon_0 > \epsilon_\infty$.

In the discussion of bipolarons, often the ratio

$$\eta = \epsilon_\infty/\epsilon_0 \tag{25}$$

of the electronic and static dielectric constant is used ($0 \leq \eta \leq 1$). It turns out that bipolaron formation is favored by smaller η.

To estimate the order of magnitude of the quantities involved, one may express α and U as follows:

$$\alpha = \sqrt{\lambda}(1/\epsilon_\infty - 1/\epsilon_0), \tag{26a}$$

$$U = \sqrt{2\lambda}(1/\epsilon_\infty), \tag{26b}$$

with

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

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

$$R_y^* = m_b e^4/2\hbar^2. \tag{27}$$

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

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

This is the generalization to bipolarons of the scaling relation for a single Fröhlich polaron (Peeters and Devreese, 1987). Physically the scaling relation implies that bipolaron formation will be facilitated in 2D as compared with 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 an analytical strong-coupling asymptotic expansion in inverse powers of the electron–phonon coupling constant for the large bipolaron energy at $T = 0$:

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

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

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

and for $B(u)$ see the above-cited paper.

The scaling relation (28) allows one to find the bipolaron energy in two dimensions as

$$E_{2D}(\alpha,u) = \tfrac{2}{3}E_{3D}\left(\frac{3\pi}{4}\alpha,u\right). \tag{30}$$

A "phase diagram" for the polaron–bipolaron system was introduced by VPD. 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 and 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.

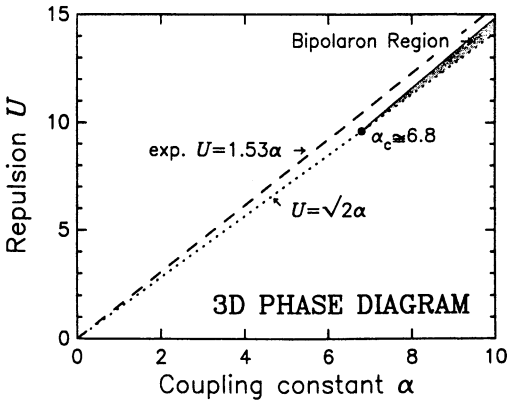

FIG. 11. The stability region for bipolaron formation in 3D from Verbist *et al.* (1990). The dotted line $U = \sqrt{2\alpha}$ separates the physical region ($U \geq \sqrt{2\alpha}$) from the nonphysical ($U \leq \sqrt{2\alpha}$). The stability region lies below the full curve. The shaded area is the stability region in physical space. The dashed line is determined by $U = \sqrt{2\alpha}/(1 - \epsilon_\infty/\epsilon_0)$ where we took the experimental values $\epsilon_\infty = 4$ and $\epsilon_0 = 50$. The critical point $\alpha_c = 6.8$ is represented as a full dot.

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 that 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 VPD.

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 VPD tend to confirm each other.

The bipolaron was also approached (Hiramoto and Toyozawa, 1985) in the path-integral representation using a special case of the trial action of VPD; 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 of VPD can be adequately formulated analytically for all α, for which the bipolaron is stable.

A very clear representation of experimental evidence 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.

Recently, the effect of a high magnetic field on bipolarons was examined both for singlet and triplet states (Fomin and Devreese, 1995).

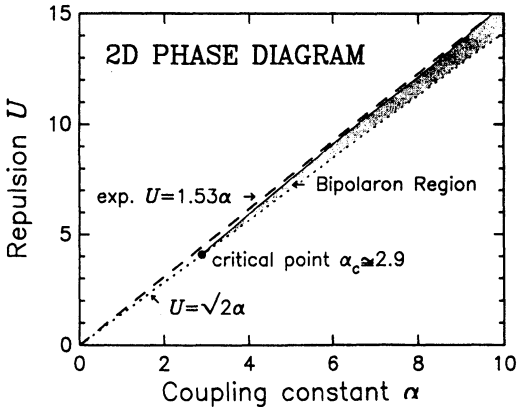

FIG. 12. The same as Fig. 11, but now for 2D, where the critical point is $\alpha_c = 2.9$; from Verbist *et al.* (1990).

3.2 Polaronic Excitons

Excitons (*q.v.*) 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 and Baldereschi, 1973; Bassani and Pastori Parravicini, 1975; Adamowski *et al.*, 1981; Wallis and Balkanski, 1986).

The exciton ground-state energy in a polar crystal was determined by Pollmann and Büttner (1975, 1977) and by Aldrich and Bajaj (1977) taking into account the fact that the potential energy of the electron–hole interaction depends on the quantum state of the interacting particles as a result of 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 a 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. Experimental data on the 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 as due to an exciton-mediated bipolaronic mechanism. Recent experimental data on the reflectivity and its temperature dependence in La_2CuO_4 were interpreted in terms of polaronic excitons by Falck *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 neighboring 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 that arises if both the Coulomb repulsion and the electron (hole)–phonon or polaron interaction are taken into account. If the polaron interaction dominates ($U_{\text{eff}} < 0$) the Coulomb repulsion, one speaks of *negative-U behavior* 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 antibonding) 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), and 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 oxides including Ti oxides, vanadium bronzes, $LiNbO_3$, and 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 to a certain critical temperature (Ranninger, 1994), which seems to be relevant to the phenomena occurring in cuprates, bismuthates, and fullerenes.

4. SPIN POLARONS

Just as 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

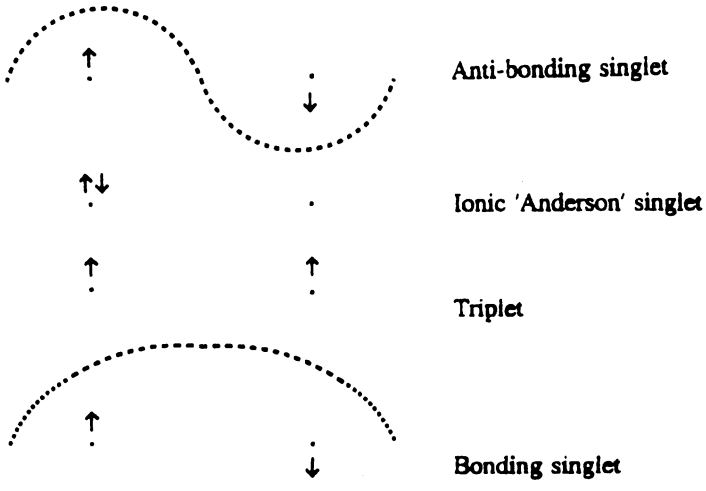

FIG. 13. States of a model two-site, two-electron system where the electrons are coupled to the interatomic coordinate; from Fisher *et al.*, (1989), reproduced by courtesy of Institute of Physics Publishing.

materials with preference for antiferromagnetic alignment; the kinetic energy of a carrier can be reduced if reversing the spins of the surrounding ions 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 $\frac{5}{2}$ 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

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

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

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

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

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, and a the lattice parameter of the host solid.

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

$$m^*_{sp} = m^* e^{\gamma R/a}, \tag{33}$$

with $\gamma \approx 1$.

5. BIPOLARONS AND HIGH-TEMPERATURE SUPERCONDUCTIVITY

Dielectric or Fröhlich bipolarons as well as spin bipolarons have been considered as possibly playing 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 behavior 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 $\mathbf{k}$ 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 spins on nearest-neighbor sites] and small bipolarons in narrow bands and characterized by hopping conductivity were still studied (Alexandrov and 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 in the superconducting phase 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 the existence line for bipolarons in $YBa_2Cu_3O_6$ corresponds to $U \approx 1.49\alpha$. 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 is shown in the figure. Presumably the Fröhlich coupling is large enough in these materials that their α overlaps with the bipolaron existence region with reference to α. It is remarkable that the existence line for bipolarons lies very close to (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 in the normal phase; see Verbist *et al.* (1990) and Devreese *et al.* (1994).

It should be reiterated 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) and 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 (Devreese *et al.*, 1994); 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 the existence of strong-coupling large Fröhlich bipolarons.)

In discussing 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.* (1994a) have also analyzed the nondegenerate gas of bosons above T_c. In particular, the linear T behavior 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 behavior 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.

A 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), based 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 the 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 $YBa_2Cu_3O_{7-\delta}$.

Also, the Cooper pairing of small polarons has been regarded as a possible mechanism of high-T_c 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 at-

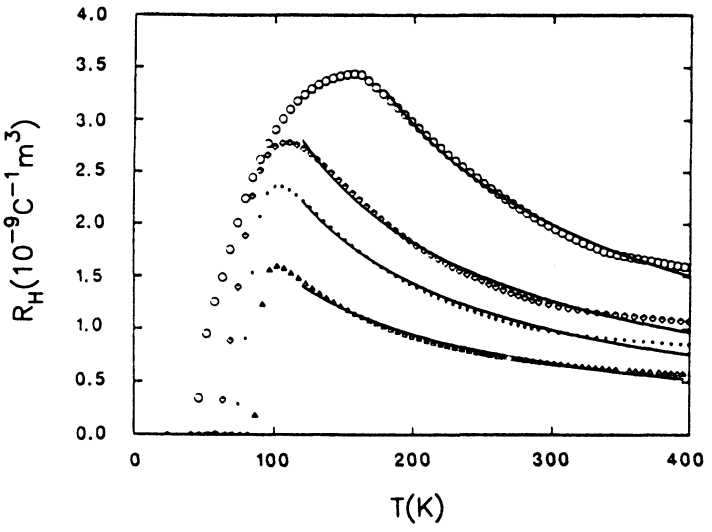

FIG. 14. Hall coefficient of $YBa_2Cu_3O_{7-\delta}$ for various degrees of reduction: $\delta = 0.05$ (△), $\delta = 0.19$ (●), $\delta = 0.23$ (◇), $\delta = 0.39$ (○) (Carrington *et al.*, 1993) in comparison with theory; from Alexandrov *et al.*, (1994b), reproduced by courtesy of Elsevier Science Publishers.

traction due to their interaction with the lattice) is smaller than, or of the same order as, the small-polaron bandwidth, both being less than or comparable to the phonon frequency. In this region, the BCS theory predicts superconductivity even for on-site repulsion, provided that it is weaker than the total intersite attraction of small polarons. It is the *polaronic narrowing* of the band that increases the estimated maximum value for the critical temperature when the interaction with high-frequency phonons is dominant. This maximum occurs for an 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 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 ground state of the system of small polarons can be—in 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 devel-

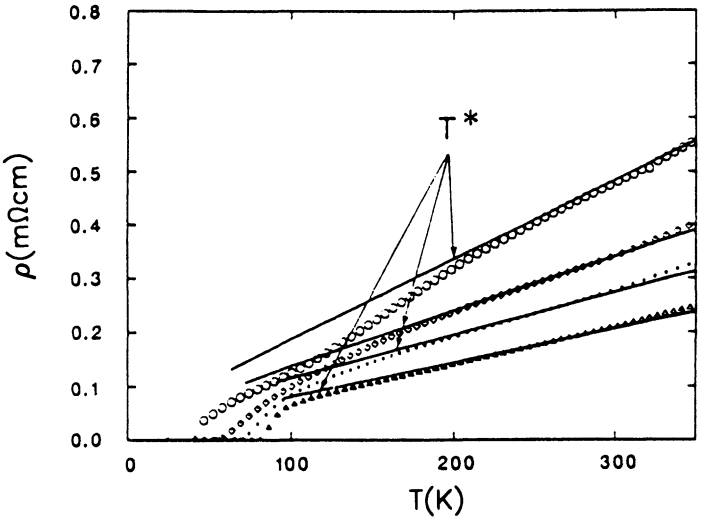

FIG. 15. Resistivity of $YBa_2Cu_3O_{7-\delta}$ for various degrees of reduction in the same denotations as in Fig. 14 (Carrington *et al.*, 1993) in comparison with theory. T^* stands for the temperature at which the change in the slope of resistivity occurs; from Alexandrov *et al.* (1994b), reproduced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

oped 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 BCS-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) has 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, nonlinear behavior, characteristic of solitons, is revealed. Polaron-type excitations were experimentally observed in polyacetylene by Su and Schrieffer (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 Modeling 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—this is a name for a quasiparticle arising from the piezoelectric interaction between an electron and acoustic phonons—were displayed by Mahan (1972) and Lax (1972). More recently, convincing experimental evidence on the significant role of piezopolarons in the electronic transport properties of CdS has been presented by Mahan (1990).

Other examples include the motion of a ^{3}He atom through superfluid helium considered by Bardeen *et al.* (1969) and by Brosens *et al.* (1991), or the dynamics of electrons (2DEG) at the surface of liquid He—"ripplonic polaron" (Jackson and Platzman, 1981; Peeters, 1987).

Charges moving through liquids (many of which are characterized by polarizable atoms) have been modeled as "hydrated polarons" (Laria *et al.*, 1991). Even an electron in-

Table 4. Extensions of the polaron concept.

Concept	"Candidates"
Acoustic polaron	Hole in AgCl
Piezoelectric polaron	ZnO, ZnS, CdS
Electronic polaron	Band structure 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 oxides, polyacetylenes
Superconductivity and (bi)-polarons ("Localized electron pairs")	$BaPb_{1-x}$ (1981) Bi_xO_3 $LiTi_2O_4$ (1985) "High-T_c superconductivity"

teracting with plasmons ("plasmaron") was invoked to study the electron gas. A new subject concerns the occurrence of polarons in fullerenes (Matus *et al.*, 1992).

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 band gap of an insulator or semiconductor is calculated using pseudopotentials. For example if one calculates, with Hartree–Fock theory, the band gap of an alkali halide, one is typically off by a factor of 2. This was the original problem that 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 that seem to be due to the electronic polaron coupling (Devreese *et al.*, 1972). The standard "local density approximation" (LDA) does not provide the correct band gap for semiconductors. The solution to this problem (Hybertsen and 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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GLOSSARY

Anderson Bipolaron: See **Intrasite Bipolaron.**

Bipolaron: A composite quasiparticle consisting of a bound state of two conduction electrons (or holes) and the surrounding common cloud of virtual phonons.

Electronic Polaron: A quasiparticle that arises as a result of the interaction between a charge carrier and the exciton field.

Ferron: See **Magnetic Polaron.**

Free Bipolaron: A **bipolaron** characterized by translational invariance, which can move as a free particle of enhanced mass (bipolaron mass).

Free Polaron: A **polaron** characterized by translational invariance, which can move as a free particle of enhanced mass (polaron mass).

Fröhlich Bipolaron: A **large bipolaron** formed through the electron–LO-phonon interaction in a polarizable continuum.

Fröhlich Polaron: A **large (radius) polaron** formed through the electron–LO-phonon interaction in a polarizable continuum.

Heitler–London Bipolaron: A singlet **intersite bipolaron.**

"Hydrated Polaron": A quasiparticle modeling charges that move through liquids (many of which are characterized by polarizable atoms).

Intersite Bipolaron: A **bipolaron** in which the two constituent small polarons are localized at two different lattice sites.

Intrasite Bipolaron: A **small bipolaron** in which the two constituent polarons are localized at the same lattice site.

Large Bipolaron: A **bipolaron** with a **Radius** much larger than the lattice constant.

Large (Radius) Polaron: A **polaron** with a radius considerably larger than the lattice constant of the solid.

Landau Polaron: See **Fröhlich Polaron.**

Magnetic Polaron: A quasiparticle consisting of an electron together with a group of magnetic moments oriented antiparallel to the electron spin as a result of the exchange interaction of the electron with the magnon field.

Pekar Polaron: See **Fröhlich Polaron.**

Piezopolaron: A quasiparticle arising from the piezoelectric interaction between an electron and acoustic phonons.

"Plasmaron": A quasiparticle sometimes considered as consisting of an electron (or hole) interacting with plasmons in the electron gas.

Polaron: A quasiparticle consisting of a conduction electron (or hole) together with

- its self-induced polarization in a polar semiconductor or an ionic crystal;
- the self-induced lattice deformation field in a nonionic material;
- the self-induced perturbation of a Bose field (in the modern extensions of the polaron concept).

Polaronic Exciton: A composite quasiparticle, which is formed by two charge carriers of opposite sign and a surrounding cloud of virtual phonons.

Radius of a bipolaron: A characteristic size of the common cloud of virtual phonons, surrounding two electrons (or holes) in a **bipolaron.**

Radius of a polaron: A characteristic size of the fluctuations in space of an electron in a **polaron** due to emission and absorption of virtual phonons.

"Ripplonic Polaron": A quasiparticle describing the dynamics of electrons at the surface of liquid ^{4}He.

Small Bipolaron: A **bipolaron** with a **radius** of the order of the lattice constant. A small bipolaron can move by hopping from one localization position to another.

Small (Radius) Polaron: A **polaron** with a radius of the order of the lattice constant. A small polaron can move by hopping from one lattice site to another.

Spin Polaron: See **Magnetic Polaron.**

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