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Spectral properties of small-polaron systems

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Small polarons, being composite particles in which the charge degrees of freedom and the lattice vibrational modes are locked together, show unique features in their single-particle spectral properties. The occupation number $n_{\mathbf{k}}$ of the polaronic charge carriers is finite and roughly constant throughout the entire Brillouin zone; with only a small jump at k_F. Strongly temperature-dependent incoherent contributions to the photoemission spectrum and the occurrence of a polaron-induced vibrational mode in the neutron scattering cross section are indications for small polarons in band states.

It is of vital importance for our understanding of strong-coupling electron-phonon systems and their superconductivity to know if, in principle, small polarons can exist as itinerant band states. There is a great deal of experimental evidence for localized polaronic states or polarons moving via thermal activation. In $Mo_xW_{1-x}O_3$,[1] however, there is some indication that below a certain characteristic temperature ~ 150 K the activated conductivity abruptly changes into a temperature-independent conductivity which could be an indication for itinerant polarons.

In spite of a huge literature,[2] the present state of the art of transport theory for small polarons does not permit one to draw any definite conclusions about the possibility of itinerant polaronic states. In this article we propose a number of experimental tests—based on robust spectral properties of the single-polaron response function—which should enable one to ascertain without ambiguity if polarons are in itinerant states or not. These tests concern the angle resolved photoemission spectroscopy (ARPES) and inelastic neutron scattering.

Upon increasing the electron-phonon coupling beyond a certain characteristic value, electrons and phonons become locked together and form new states: the small polarons. The electrons and phonons are then nothing but their elementary excitations. The itinerant (respectively, nonitinerant character of small polarons) reflects itself in the composition of these polaronic states, and becomes manifest in the specific properties of the electronic and vibrational excitations in such systems.

In the extreme limit of strong electron-phonon coupling, small polarons are expected to form band states with much reduced bandwidth. With decreasing electron-phonon coupling such a small-polaron band, contrary to a wide spread belief, does *not* go over smoothly into the band of quasi-free electrons in the weak-coupling limit, as was shown by us.[3] The transition between quasi-free electrons and small polarons is known to occur abruptly within a small regime of the electron-phonon coupling constant.[4] Exact diagonalization studies of the polaron problem on small clusters[3] suggest that the lowest energy branch of the polaronic band states is well defined not only in the extreme strong-coupling limit $\alpha \to \infty$, but all the way down to $\alpha \geq 1$; as soon as polaron formation sets in. Higher branches of the polaron band states, separated from the lowest branch by multiples of the characteristic phonon frequency ω_0, become well defined only for increasingly higher values of α. For the purpose of the present study we shall limit ourselves to temperatures small compared to ω_0. We then can use the standard polaron theory in order to study the spectral properties of small polarons. As we shall show below, we expect the following features which distinguish itinerant from nonitinerant small polarons:

(i) A distribution function of the charge carriers as a function of wave vector $\mathbf{k}$ which fills the entire Brillouin zone, with only a small step at the Fermi vector $\mathbf{k}_F$.

(ii) An ARPES spectrum which differs from that of Franck-Condon processes by strongly temperature-dependent amplitudes and peak positions of multiphonon resonances in the incoherent part of the spectrum.

(iii) The appearance of a low frequency, large amplitude "phonon mode" which puts an upper bound on antiadiabaticity.

As the basis for our study we choose the simplest generic model describing small polarons which is the Holstein molecular crystal model defined by

$$H = t\sum_{i,\sigma} n_{i\sigma} - t \sum_{\langle i \neq j \rangle,\sigma} c_{i\sigma}^{\dagger} c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} - \lambda \sum_{i,\sigma} n_{i\sigma} u_i + \frac{M}{2} \sum_i (\dot{u}_i^2 + \omega_0^2 u_i^2) \, . \tag{1}$$

t denotes the bare electron hopping integral, λ the electron-phonon coupling constant, U the onsite Coulomb repulsion, M the mass of the ions and u_i the displacements from their equilibrium positions. The electron annihilation (creation) operators at molecular sites i and spin σ are described by $c_{i\sigma}^{(+)}$ and $n_{i\sigma} = c_{i\sigma}^{\dagger} c_{i\sigma}$. We choose deliberately a system of uncoupled Einstein oscillators (having frequency ω_0) in order to clearly show how these oscillators become correlated in the case of coherent itinerant polaron motion which is of the origin of a new "phonon mode."

The basic starting point for small-polaron theory is the assumption of rather well-defined local polaronic states: $|1\sigma\rangle_i^n = c_{i\sigma}^{\dagger}|0\rangle |\phi(\mathbf{x}-\mathbf{x}_0)\rangle_i^n$ with n phonon modes excited. These states can be superposed to form Bloch states,

which for zero phonon excitations read

$$|1\sigma)_\kappa^0=\frac{1}{\sqrt{N}}\sum_i e^{i\kappa r_i}c_{i\sigma}^\dagger|0\rangle|\phi(\mathbf{x}-\mathbf{x}_0)\rangle_i^0\prod_{j\neq i}|\phi(\mathbf{x})\rangle_j^0 . \quad (2)$$

$|\phi(\mathbf{x}-\mathbf{x}_0)\rangle_i^0$ denotes an harmonic oscillator state for a molecular unit at site i whose intramolecular distance is shrunk by $|\mathbf{x}_0|=\lambda/M\omega_0^2$.

The formal theory for small polarons is largely based on the Lang-Firsov approach,[2] a unitary transformation, of the form

$$S=\exp\left[\sum_i\frac{\lambda(a_i-a_i^\dagger)(n_{i\uparrow}+n_{i\downarrow})}{\hbar\omega_0(2M\omega_0/\hbar)^{1/2}}\right], \quad (3)$$

which transforms the original Hamiltonian [Eq. (1)] into

$$\begin{aligned}\tilde{H}&=S^{-1}HS=H_{\rm pol}+H_{\rm int}+H_{\rm pol,ph}\ ,\\ H_{\rm pol}&=\sum_{i,\sigma}(t-\varepsilon_p)n_{i\sigma}-t^*\sum_{\langle i\neq j\rangle,\sigma}c_{i\sigma}^\dagger c_{j\sigma}\\ &\quad+\sum_i\hbar\omega_0(a_i^\dagger a_i+\tfrac{1}{2})\ , \quad (4)\\ H_{\rm int}&=(U-v)\sum_i n_{i\uparrow}n_{i\downarrow},\\ H_{\rm pol,ph}&=-\sum_{\langle i\neq j\rangle,\sigma}(\hat{\sigma}_{ij}-t^*)c_{i\sigma}^\dagger c_{j\sigma}\ .\end{aligned}$$

$H_{\rm pol}$ describes the main qualitative features of free small polarons: the shift in the harmonic oscillator positions propositional to $|\mathbf{x}_0|$, the polaron level shift $\varepsilon_p=\lambda^2/2M\omega_0^2\equiv\alpha^2\omega_0$ and the polaron hopping integral $t^*=te^{-\alpha^2}$. The eigenstates corresponding to $H_{\rm pol}$ are the Bloch states given by Eq. (2). $H_{\rm int}$ describes the polaron-polaron interaction with an attractive renormalization induced by the polaronic mechanism. Finally, $H_{\rm pol,ph}$ describes the residual interaction between the polaronic band states and phonons where

$$\hat{\sigma}_{ij}=t\exp\left\{\frac{\varepsilon_p}{\hbar\omega_0}[(a_i-a_i^\dagger)-(a_j-a_j^\dagger)]\right\}. \quad (5)$$

$t^*\equiv\langle\hat{\sigma}_{ij}\rangle$ denotes $\hat{\sigma}_{ij}$ averaged with respect to the free phonon Hamiltonian, the last term in $H_{\rm pol}$ [Eq. (4)] where the phonon operators at molecular sites i are defined by $u_i=(a_i+a_i^\dagger)/(2M\omega_0/\hbar)^{1/2}$.

We shall consider here only the case where small polarons are stable against bipolaron formation. This happens when the polaron-polaron attraction v is roughly compensated by the Coulomb repulsion U. The single particle Green's function for the electrons evaluated to second order in $H_{\rm pol,ph}$ (Ref. 5) then reads

$$\begin{aligned}G(\mathbf{k},\omega_n)&=\frac{e^{-\alpha^2}}{i\omega_n-\xi_{\mathbf{k}}}\\ &\quad+e^{-\alpha^2}\sum_l\frac{\alpha^{2l}}{l!}\frac{1}{N}\sum_{\mathbf{k}'}\left[\frac{n(\xi_{\mathbf{k}'})}{i\omega_n-\xi_{\mathbf{k}'}+l\omega_0}\right.\\ &\quad\left.+\frac{1-n(\xi_{\mathbf{k}'})}{i\omega_n-\xi_{\mathbf{k}'}-l\omega_0}\right]. \quad (6)\end{aligned}$$

ω_n denotes the Matsubara frequencies, the polaron energy $\xi_{\mathbf{k}}=\varepsilon_{\mathbf{k}}-\mu$ is measured from the polaron chemical potential μ and $n(\xi_{\mathbf{k}})$ denotes the Fermi distribution function.

From expression (6) we immediately obtain the distribution function of the electrons in a many polaron system:

$$n_{\mathbf{k}\sigma}=\langle c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma}\rangle=(1-e^{-\alpha^2})n_\sigma+e^{-\alpha^2}n_\sigma(\xi_{\mathbf{k}}) , \quad (7)$$

where n_σ is the total number density of polarons with spin σ. We notice that $n_{\mathbf{k}\sigma}$ is constant throughout the Brillouin zone apart from a small jump equal to $e^{-\alpha^2}$ at $k=k_F$ (see Fig. 1). This result is expected for sufficiently large α where small-polaronic band states (2) exist and for which the incoherent part of the one electron Green's function is $\mathbf{k}$ independent.

Exact diagonalization studies[3] for small clusters show that the incoherent part of the one particle Green's function becomes increasingly $\mathbf{k}$ dependent and diminishes strongly as α is lowered towards a critical value where small polarons become unstable towards quasi-free electrons. The random-phase approximation (RPA) result (6) for the one electron Green's function with its $\mathbf{k}$-independent incoherent contribution reflects the physics in the strong-coupling polaronic limit leading to the particular shape of $n_{\mathbf{k}\sigma}$ depicted in Fig. 1. From the numerical analyses of the one particle Green's function[3] we conjecture that the form of $n_{\mathbf{k}\sigma}$ will evolve in the following way upon reducing α. As one approaches the limit of stability of small polarons, the jump in $n_{\mathbf{k}\sigma}$ will become increasingly larger and at the same time will get smeared out over an interval ω_0 around the Fermi energy. $n_{\mathbf{k}\sigma}$ then resembles that expected for a marginal Fermi liquid. Upon further decreasing α, the jump in $n_{\mathbf{k}\sigma}$ further increases becoming of order unity and sharpens up as one reaches the quasi-free electron limit. One then recuperates the normal Fermi liquid distribution (see Fig. 1).

The reason for the smearing out of the electron distribution function over the entire Brillouin zone in the polaronic regime can easily be understood by rewriting the

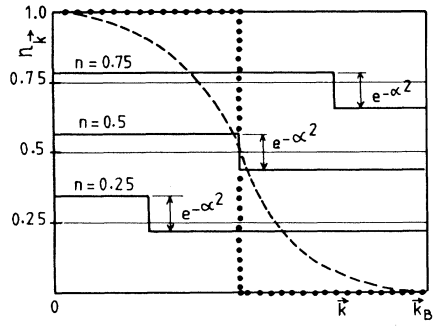

FIG. 1. Schematic representation of the occupation number of charge carriers for an itinerant polaronic system for $\alpha\gg1$ and for three cases: a quarter-filled, a half-filled, and a three quarter-filled band per spin degree of freedom. The dashed and dotted curves for half-filling represents conjectured forms of $n_{\mathbf{k}\sigma}$ for $\alpha\simeq1$ and $\alpha\ll1$, respectively.

single-polaron state $|1\sigma\rangle_\kappa^0$ [Eq. (3)] in the form:

$$|1\sigma\rangle_\kappa^0=\frac{1}{N^{3/2}}\sum_i\sum_{\mathbf{k},\mathbf{q}} e^{i(\kappa-\mathbf{k}+\mathbf{q})\mathbf{r}_i} \times c_{\mathbf{k}\sigma}^\dagger|0\rangle|\phi(\mathbf{x}-\mathbf{x}_0)\rangle_\mathbf{q}^0\prod_{j\neq i}|\phi(\mathbf{x})\rangle_j \quad (8)$$

where

$$|\phi(\mathbf{x}-\mathbf{x}_0)\rangle_\mathbf{q}^0=\frac{1}{\sqrt{N}}\sum_i e^{i\mathbf{q}\mathbf{r}_i}|\phi(\mathbf{x}-\mathbf{x}_0)\rangle_i^0$$

describes a Bloch state of molecular deformations (variations of the intra-atomic distances) with wave vector $\mathbf{q}$. The polaronic state $|1\sigma\rangle_\kappa^0$ describing a polaron with wave vector κ hence is a superposition of electron Bloch-states with an ensemble of wave vectors $\mathbf{k}$ and deformation waves with wave vectors $\mathbf{q}$. Both $\mathbf{k}$ and $\mathbf{q}$ are distributed over the entire Brillouin zone such that the total momentum $-\mathbf{k}+\mathbf{q}=\boldsymbol{\kappa}$ is conserved. The many polaron ground state is given by $|N\rangle^0=\prod_{\kappa\leq\kappa_N}|1\sigma\rangle_\kappa^0$ where κ_N is the cutoff wave vector determined by the total number of polarons N in the system. The characteristic shape of the electron distribution function in a many polaron system [Eq. (7)] is an unambiguous signature for itinerant polaronic states.

Another feature which characterizes itinerant polarons in contrast to localized ones is the strong temperature dependence of the incoherent part of the ARPES spectrum, the intensity of which is given by

$$I(\mathbf{k},\varepsilon)=(2\pi^3\gamma^2)^{-1/2}\int d\omega e^{-(\varepsilon-\omega)^2/2\gamma^2}n(\omega)\mathrm{Im}G(\mathbf{k},\omega) \quad (9)$$

where γ denotes the width of the experimental resolution.

The temperature dependence of the ARPES spectrum is determined (i) by the smearing out of the step of $n_\mathbf{k}$ and (ii) by the displacement of the chemical potential. Upon increasing the temperature the first leads to a decrease of the amplitudes of the oscillatory part of the incoherent contribution to ARPES. The second leads to a shift of the oscillatory part towards higher (lower) binding energies depending on band-filling which is less (more) than half-filling. In Figs. 2(a) and 2(b) we plot $I(\mathbf{k},\varepsilon)$ for $\mathbf{k}=\mathbf{k}_F$ for $n=0.3$ and 0.7 for three characteristic temperatures T:23,300, and 500 K. For the half-filled band case, $n=0.5$ one observes practically no shift of the ARPES intensities since in that case μ is independent on temperature.

In contrast to the ARPES for itinerant polarons, that for localized polarons is given by

$$\sqrt{2\pi}\gamma I(\mathbf{k},\varepsilon)=\sum_{l=0}^{\infty} e^{-\alpha^2}(\alpha^{2l}/l!)\exp[-\tfrac{1}{2}(\varepsilon-l\omega_0)^2/\gamma^2] \quad (10)$$

and is plotted in Fig. 3.

In all these calculations we assumed T to be small compared to the phonon frequency ω_0. We then expect no temperature dependence for ARPES for localized polarons, contrary to that of itinerant polarons.

The parameters chosen in these calculations are

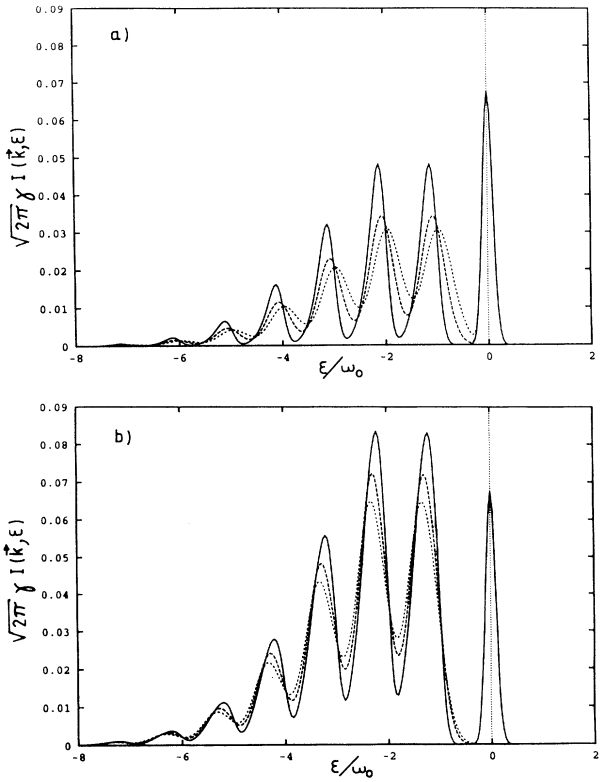

FIG. 2. Angle resolved photoemission intensity for a system of itinerant small polarons for $k=k_F$ and $T=23$ K (continuous line), 300 K (dashed line), and $T=500$ K (dotted line). (a) $n=0.3$, (b) $n=0.7$.

$W=60$ meV for the polaron band width, $\omega_0=200$ meV, $\alpha^2=2$ and $\gamma=20$ meV. This should roughly correspond to the case of M_xC_{60}, where such temperature behavior was indeed observed in angle integrated photoemission spectroscopy.[6] In these materials the electrons are strongly coupled to a breathing mode of frequency $\omega_0\sim 1500$ cm^{-1} involving the pentagons of carbon atoms in the C_{60} balls.

Finally, the third signature for itinerant small polarons which we shall discuss in this article is the appearance of a polaron induced "phonon mode."

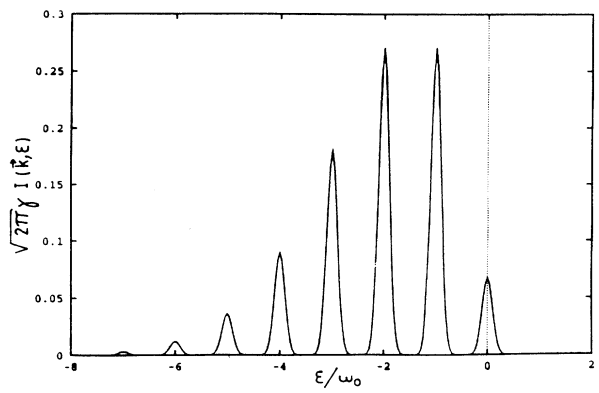

FIG. 3. Photoemission intensity for a system of localized small polarons.

For a system with randomly localized polarons, we have a set of molecules which occur in two distinct oscillator states corresponding to intramolecular distances differing by $|\mathbf{x}_0|$. If the frequency of the individual molecules is independent of the intramolecular distance [as assumed in our model, Eq. (1)], we have a set of independent Einstein oscillators with frequency ω_0. The oscillations of different molecules are uncorrelated. If instead of localized electrons we consider coherently moving electrons in this system, it requires that the motion of the electrons and the motion of the polaron induced modulations of the intramolecular distances are correlated. There is experimental evidence from optical spectroscopy which shows that the appearance of itinerant polarons accompanies such nonadiabatic behavior.[7] Such features are clearly distinct from quasiharmonic or anharmonic lattice dynamics as far as concerns the appearance of (polaron induced) modes which show unusual temperature dependence for their oscillator strength and linewidth. For a single polaron this leads to Bloch states of molecular deformations $|\phi(\mathbf{x}-\mathbf{x}_0)\rangle_{\mathbf{q}}^0$. Because of their coherence with the electron motion they have exactly the dispersion of small polarons as was shown previously.[8] For a many polaron system, because of the superposition of polaronic states with wave vector $\kappa[0,\kappa_F]$ we obtain for a given $\mathbf{q}$ a superposition of polaron energies leading to a scattering cross section for phonons with an intensity which covers a sizable fractions of the frequency regime of the polaron bandwidth. The quantity which measures those excitations is given by the phonon Green's function $\langle Ta_{\mathbf{q}}(t)a_{\mathbf{q}}^{\dagger}(0)\rangle$. Transforming this correlation function to the Hilbert space of polaronic states (via the Lang-Firsov transformation) whose dynamics is controlled by the polaron Hamiltonian, we obtain

$$\langle T(a_{\mathbf{q}}(t)-\alpha n_{\mathbf{q}}(t))(a_{\mathbf{q}}^{+}(0)-\alpha n_{\mathbf{q}}(0))\rangle \tag{11}$$

with $n_{\mathbf{q}}=\sum_{\mathbf{k},\sigma}c_{\mathbf{k}+\mathbf{q}\sigma}^{\dagger}c_{\mathbf{k}\sigma}$. The contribution $\propto\langle a_{\mathbf{q}}(t)a_{\mathbf{q}}^{\dagger}(0)\rangle$ in Eq. (11) measures the usual response of renormalized intrinsic phonons of the system. The contribution $\propto\langle n_{\mathbf{q}}(t)n_{\mathbf{q}}(0)\rangle$ on the contrary measures the response of a deformation wave induced by the itinerant motion of the polarons. This quantity is in principle measurable by either optical experiments in the limit $\mathbf{q}\rightarrow 0$ or by inelastic neutron scattering for finite $\mathbf{q}$. For the two extreme cases $\mathbf{q}\rightarrow 0$ and $\mathbf{q}=\mathbf{q}_B$ ($\mathbf{q}_B$ being a high symmetry Brillouin vector) we have[8]

$$\langle n_{\mathbf{q}}(t)n_{\mathbf{q}}(0)\rangle \propto \begin{cases} \dfrac{\omega}{|\mathbf{q}|} & \text{for } \omega<2|\mathbf{q}|a\sqrt{2\mu t^*},\ \ \mathbf{q}\rightarrow 0\ , \\ \rho\left[\dfrac{\omega}{2}\right]\theta(\omega-2\mu)\theta(W-\omega), & \mathbf{q}=\mathbf{q}_B\ , \end{cases} \tag{12}$$

where a denotes the lattice constant and $\rho(\omega)$ the polaron density of states.

The contribution (12) to the phonon Green's function is of purely electronic origin which results from the locking together of the electronic and vibrational degrees of freedom in small-polaron systems. The appearance of a deformation wave, driven by the charge fluctuations of the system, is a unique feature of itinerant small polaronic states. Their bandwidth can thus be determined by inelastic neutron scattering which is expected to yield finite intensity smeared out over an energy regime of the order of half the polaronic bandwidth. This energy regime is well below that of the energy of the intrinsic polarons in the system. For $\mathbf{q}\sim\mathbf{q}_B$ one expects a gap in the excitation spectrum.

The appearance of such low-lying lattice mode within a frequency regime of the order of the polaron bandwidth sets a limit to the degree of antiadiabaticity. The consequence of such modes on transport phenomena in polaronic systems is presently under study.

Using the fact that small polarons are composite particles in which the charge carriers and the intrinsic lattice vibrations are locked together, we showed that the dynamical properties of such small polarons are reflected in characteristic properties of their single particle spectral functions. In principle these can be tested experimentally and should unambiguously distinguish itinerant small polarons from those either localized or moving by thermal activation.

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