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Polaronic effects in the photoemission spectra of strongly coupled electron-phonon systems

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The angle-resolved photoemission spectrum is derived for systems with strong electron-phonon coupling. Polaronic features of the charge carriers are manifest in a broad spectrum, with a maximum at an energy (below the Fermi energy) corresponding to the polaron binding energy. In the strong-coupling limit and with dispersionless phonons an oscillatory structure is superposed on this broad spectrum with a frequency equal to the characteristic phonon frequency.

There is great need for decisive experiments capable of testing the polaronic nature of charge carriers in systems with strong electron-phonon interaction. The characteristic features of small polarons are theoretically well understood[1,2] and are tantamount to charge carriers which are surrounded by a fairly localized deformation field of the lattice. For a moving small polaron, there is a perpetual exchange of the momenta carried by the electron and by the deformation field. This gives rise to strong mixing of electron degrees of freedom and strongly populated phonon modes. Photoemission spectroscopy should therefore be able to detect such strong mixing of purely electronic states with lattice vibrational excitations. Analogously, inelastic neutron scattering should show up the strong coupling of phonon modes to electronic excitations. A number of experiments [x-ray photoemission spectroscopy (XPS), neutron scattering, extended-x-ray absorption-fine-structure (EXAFS) and radial distribution function, temperature dependence of Debye Waller factors, etc.] testing the polaronic features in small systems recently have been treated theoretically.[3]

In the present paper we develop a theory for angle-resolved photoemission spectroscopy (ARPES) for a system characterized by a band of small polarons. As we shall show below, ARPES is expected to show Fermi-surface features with a broad asymmetric line shape. We predict, under certain conditions, an oscillatory structure, superimposed on this broad spectrum which has a peak at an energy (below the Fermi energy) which roughly corresponds to the polaron binding energy. The oscillations of the superimposed structure have a frequency equal to the characteristic phonon frequency of the system and reflect the strong mixing of purely electronic and purely phononic degrees of freedom.

The intensity of angle-resolved XPS spectra is determined by the Fourier transform of the retarded one-particle Green's function,

$$I(\mathbf{k},\varepsilon) = -\frac{1}{\pi}\int_{-\infty}^{+\infty} d\varepsilon' n(\varepsilon')\mathrm{Im}G^R(\mathbf{k},\varepsilon')F(\varepsilon,\varepsilon') , \quad (1)$$

where $\mathbf{k}$ and ε denote the momentum and energy of the emitted electron, measured by the analyzer with a Gaussian instrumental resolution function

$$F(\varepsilon,\varepsilon') = \frac{1}{\gamma\sqrt{2\pi}}\exp\left[-\frac{1}{2}\left[\frac{\varepsilon-\varepsilon'}{\gamma}\right]^2\right] . \quad (2)$$

The present day highest resolution experiments correspond to a γ of the order of 20 meV, $n(\varepsilon)=[\exp(\varepsilon/k_BT)+1]^{-1}$. $G^R(\mathbf{k},\varepsilon)$ in Eq. (1) is obtained in the usual way by analytic continuation of the Matsubara temperature-dependent Green's function,

$$G(\mathbf{k},\omega_n) = -\frac{1}{2}\sum_{\mathbf{m}} e^{i\mathbf{k}\cdot\mathbf{m}}\int_{-\beta}^{+\beta} d\tau\, e^{i\omega_n\tau}\langle T_\tau c_{0\sigma}(\tau)c^\dagger_{\mathbf{m}\sigma}(0)\rangle , \quad (3)$$

to the upper half plane of $\omega_n = i\pi n/\beta$, n being an odd integer and $\beta=(1/k_BT)$. $c_{\mathbf{m}\sigma}(c^\dagger_{\mathbf{m}\sigma})$ denote electron annihilation (creation) operators on sites $\mathbf{m}$ and spin σ. Applying the standard Holstein-Lang-Firsov transformation,[2] the bare Fröhlich Hamiltonian H can be written in the form[4]

$$\tilde{H} = e^S H e^{-S} = \sum_{\substack{\mathbf{m},\mathbf{n}\\ \sigma\sigma'}} [\sigma(\mathbf{m}-\mathbf{n},+0)T(\mathbf{m}-\mathbf{n})\delta_{\sigma\sigma'}c^\dagger_{\mathbf{m}\sigma}c_{\mathbf{n}\sigma} + v(\mathbf{m}-\mathbf{n})n_{\mathbf{m}\sigma}n_{\mathbf{n}\sigma'}] + \sum_{\mathbf{q}}\omega(\mathbf{q})d^\dagger_{\mathbf{q}}d_{\mathbf{q}} , \quad (4)$$

where

$$S = \frac{1}{\sqrt{2N}}\sum_{\substack{\mathbf{q},\mathbf{m}\\ \sigma}}\gamma(\mathbf{q})(d_{\mathbf{q}}e^{i\mathbf{q}\cdot\mathbf{m}} - d^\dagger_{\mathbf{q}}e^{-i\mathbf{q}\cdot\mathbf{m}})n_{\mathbf{m}\sigma}$$

$$\sigma(\mathbf{m},\tau) = \left\langle T_\tau \exp\left[\frac{1}{\sqrt{2N}}\sum_{\mathbf{q}}\gamma(\mathbf{q})[d^\dagger_{\mathbf{q}}(\tau)e^{i\mathbf{q}\cdot\mathbf{m}} - d_{\mathbf{q}}(\tau)e^{-i\mathbf{q}\cdot\mathbf{m}}]\right]\exp\left[\frac{1}{\sqrt{2N}}\sum_{\mathbf{q}}\gamma(\mathbf{q})(d_{\mathbf{q}}-d^\dagger_{\mathbf{q}})\right]\right\rangle . \quad (5)$$

$T(\mathbf{m}-\mathbf{n})$ denotes the bare hopping integral and $v(\mathbf{m}-\mathbf{n})$ the induced polaron-polaron interaction, which may be attractive and giving rise to small bipolaron formation.[4] $\omega(\mathbf{q})$ is the phonon frequency of wave vector $\mathbf{q}$, $\gamma(\mathbf{q})$ denotes the matrix element for electron-phonon interaction, $n_{\mathbf{m}\sigma}=c^\dagger_{\mathbf{m}\sigma}c_{\mathbf{m}\sigma}$, and N is the number of lattice sites.

Applying the Holstein-Lang-Firsov transformation to the single-electron Green's function, Eq. (3), we can express the single-particle Green's function [Eq. (3)] in terms of polaron operators $\tilde{c}_{m\sigma}=e^{S}c_{m\sigma}e^{-S}$ and thus obtain

$$G(\mathbf{k},\omega_n)=\frac{k_BT}{N}\sum_{\omega_{n'}}\sum_{\mathbf{m},\mathbf{k}'}\sigma(\mathbf{m},\omega_{n'}-\omega_n)G_p(\mathbf{k}',\omega_{n'})\times e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{m}}. \quad (6)$$

$G_p(\mathbf{k},\omega_{n'})$ denotes the single-polaron Green's function (see below) and $\sigma(\mathbf{m},\omega_n)$ describes the Green's function for the phonon cloud which accompanies the motion of the electron. Expression (6) is obtained after averaging over the free-phonon Hamiltonian which neglects retardation effects. If one treats the polaron-polaron interaction in the Hamiltonian $\tilde{H}$, Eq. (4), in the simplest way—the Hartree approximation—one obtains

$$G_p(\mathbf{k},\omega_n)=(i\omega_n-\xi_{\mathbf{k}})^{-1} \quad (7)$$

with an energy dispersion $\xi_{\mathbf{k}}=\sum_{\mathbf{m}}\sigma(\mathbf{m},0)T(\mathbf{m})e^{i\mathbf{k}\cdot\mathbf{m}}-\mu$ for the polaronic band having a narrowed band half-width $W=D\sigma\ll D$ [where $D=zT(\mathbf{m})$ is the bare band half-width and z the coordination number]. Thus, small polarons have a well-defined Fermi surface which is simply a replica of that the bare electrons (in a rigid lattice) but with a very much reduced Fermi energy.

The correlation function $\sigma(\mathbf{m},\tau)$ is obtained using the Lang-Firsov technique:[5]

$$\sigma(\mathbf{m},\tau)=\exp\left\{-\frac{1}{2N}\sum_{\mathbf{q}}\gamma^2(\mathbf{q})\left[\coth\left(\frac{\omega(\mathbf{q})}{2k_BT}\right)\{1-\cos(\mathbf{q}\cdot\mathbf{m})\cosh[\omega(\mathbf{q})\tau]\}+\cos(\mathbf{q}\cdot\mathbf{m})\sinh[\omega(\mathbf{q})|\tau|]\right]\right\}. \quad (8)$$

Taking the Fourier component of Eq. (8) and substituting it together with Eq. (7) into Eq. (6) one obtains

$$G(\mathbf{k},\omega_n)=\frac{e^{-g^2}}{i\omega_n-\xi_{\mathbf{k}}}+\frac{e^{-g^2}}{N}\sum_{l=1}^{\infty}\frac{g^{2l}}{l!}\times\sum_{\mathbf{k}'}\left[\frac{n(\xi_{\mathbf{k}'})}{i\omega_n-\xi_{\mathbf{k}'}+l\omega_0}+\frac{1-n(\xi_{\mathbf{k}'})}{i\omega_n-\xi_{\mathbf{k}'}-l\omega_0}\right]. \quad (9)$$

Equation (9) is the result for the simplest case, i.e., molecular dispersionless vibrations ($\omega=\omega_0$) and $\mathbf{q}$-independent coupling $\gamma^2(\mathbf{q})=2g^2$. Moreover, we take the limit $T\ll\omega_0$.

Expression (9) consists of two physically distinct terms. The first arises from a polaronic band describing coherent tunneling of electrons and their surrounding phonon cloud. The factor e^{-g^2} plays the role of Z in a Fermi-liquid description and determines the jump in the Fermi distribution function. The second contribution in expression (9) describes the possibility of changing the number of phonons in the phonon cloud during the excitation of the electron. It is this term which will characteristically influence the photoemission spectrum in polaronic systems. Notice that this term contains the sum over all electron momenta which reflects the fact, as already remarked above, that the electron momentum is not conserved separately. The fact that this second term in Eq. (9) does not show any $\mathbf{k}$ dependence is due to the approximation made in deriving Eq. (6). As has been shown analytically,[5] starting from the strong (∞) coupling limit, a perturbation expansion in terms of the inverse coupling strength gives rise to negligible damping and frequency renormalization effects. Moreover, exact numerical diagonalization procedures treating the polaron problem on small clusters[3] show that for large coupling one should not expect any $\mathbf{k}$ dependence of this second term in ARPES intensity. Such $\mathbf{k}$ dependence will become important, however, as one approaches the critical coupling strength $g^2\omega_0/D>1/\sqrt{2z}$ from above.[3] We shall defer the discussion of these rather detailed questions to a future work. In the present paper let us concentrate on the main features of the characteristic properties of ARPES which we expect for polaronic systems.

We notice that the electronic spectral density in the second term in Eq. (9) spreads over a wide frequency range of the order of the polaron binding energy $\sim g^2\omega_0$. This strongly contrasts with the first term in Eq. (9), the purely polaronic band contribution, which has a characteristic frequency range of the order of the polaron band half-width W. Making the analytic continuation $i\omega_n\rightarrow\varepsilon+i\delta$ in Eq. (9) we obtain the final result for the angle- and energy-dependent intensity of photoemission spectra:

$$I(\mathbf{k},\varepsilon)=\frac{1}{\gamma\sqrt{2\pi}}n(\xi_{\mathbf{k}})e^{-g^2}\exp\left[-\frac{1}{2}\left(\frac{\varepsilon-\xi_{\mathbf{k}}}{\gamma}\right)^2\right]+\int_{-\infty}^{+\infty}d\varepsilon'\,F(\varepsilon,\varepsilon')e^{-g^2}\sum_{l=1}^{\infty}\frac{g^{2l}}{l!}N_p(\varepsilon'+l\omega_0)n(\varepsilon'+l\omega_0), \quad (10)$$

where $N_p(\varepsilon)=1/N\sum_{\mathbf{k}'}\delta(\xi_{\mathbf{k}'}-\varepsilon)$ is the polaronic density of states.

The first term in Eq. (10) describes the binding energy (ε) dependence of the photoemission from the polaronic band for different angles (different $\xi_{\mathbf{k}}$). The second term describes the angle-independent line shape due to the phonon-assisted photoemission.

In Figs. 1–3 we present the binding-energy-dependent photoemission spectra as determined from Eq. (10) for three angles characterized by $\xi_{\mathbf{k}}/\omega_0=0$ and ±0.5 and different coupling strengths g^2. As one can see from Fig. 2 the broadened asymmetric line shape occurs already for $g^2=1$. This result (Fig. 2) agrees with the qualitative prediction by Sawatzky (see the dashed line in Fig. 2 of Ref. 6) for lifetime effects in the ARPES of electrons, strongly coupled to phonons or magnons. For $g^2\geq2$ and $D=200$ meV, the polaronic bandwidth W starts to be smaller than the phonon frequency ω_0. In this nonadiabatic regime ($W\leq\omega_0$) the second contribution in Eq. (10) oscillates as a function of ϵ with the characteristic

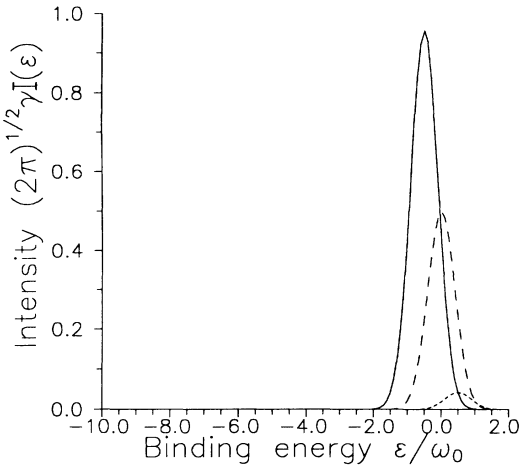

FIG. 1. ARPES for three angles, corresponding to $\xi_k/\omega_0 = -0.5$ (solid line), $\xi_k/\omega_0 = 0.5$ (dotted line), and $\xi_k = 0$ (dashed line) for uncoupled electrons; $\gamma = 20$ meV, $\omega_0 = 50$ meV, $T = 90$ K.

energy equal to ω_0 and the photoemission spectrum starts to resemble that of gaseous hydrogen.[7] To obtain Figs. 2 and 3 we used a Gaussian density of states for polarons $N_p(\varepsilon)$ with the width W. Due to the extreme narrowness of the polaronic band, $W \lesssim \omega_0$, the exact form of $N_p(\varepsilon)$ does not play any role.

In conclusion, we derived the angle-resolved photoemission spectrum for a strongly coupled electron-phonon system. In the polaronic regime we obtain a broadened asymmetric line shape with a width of the order of $g^2\omega_0$ and Fermi-liquid features near the chemical potential, arising from the coherent motion of the polarons (Figs. 2 and 3). The incoherent quasicontinuum shows oscillations with a characteristic phonon frequency in the case of dispersionless phonons and strong coupling, when the polaronic bandwidth is sufficiently narrow. The sum rule is violated if one takes only the coherent part of the ARPES, described by the first term in Eq. (10), but holds, of course, as far as the entire spectrum is concerned.

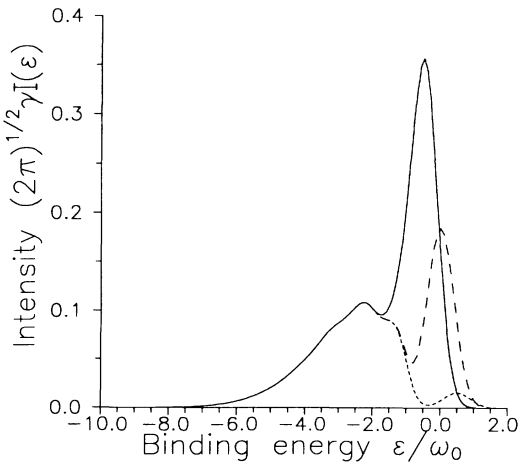

FIG. 2. ARPES for $g^2 = 1$, $\gamma = 20$ meV, $\omega_0 = 50$ meV, $T = 90$ K, $D = 200$ meV.

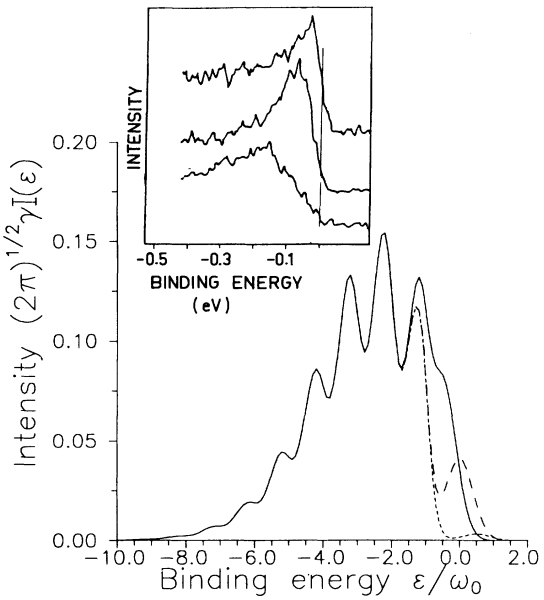

FIG. 3. ARPES for $g^2 = 2.5$; the other parameters are the same as in Fig. 2. Inset: Experimental results following Ref. 9.

In order to understand the mechanism leading to high-temperature superconductivity it is essential to have a precise knowledge of the nature of charge carriers in the normal state. Detailed high-resolution photoemission spectroscopy[8,9] can, in principle, answer the key question: whether or not the normal state of the metal oxides is a Fermi liquid. ARPES (Ref. 9) gives strong support for the existence of quasiparticles with a Fermi surface which is largely in agreement with the canonical band-structure calculation. Yet there are puzzling features such as the broad (> 100 meV) asymmetric line shape,[8,9] the apparent violation of the sum rule[8] and the temperature dependence of photoemission spectra.[8] In view of the difficulties of a Fermi-liquid description of the low-frequency kinetics and thermodynamics of metal oxides,[10] the interpretation of the ARPES remains a matter of controversy.[11] Such interpretations were based so far on the electron correlation approach to high-temperature superconductivity. Our present study shows that ARPES in high-T_c oxides (Fig. 3, inset) may be compatible with the picture of small polarons as intrinsic charge carriers in these materials. Of course, the oscillations of the experimental spectrum in $Bi_2Sr_2CaCu_2O_8$ is not so regular (or perhaps not at all existent) as predicted by Eq. (10). However, such oscillations have been observed recently in gaseous C_{60}.[12] One should remember that there may be several characteristic ω_0's in the real materials with the different coupling strength g for each mode, so the oscillatory behavior may be very different. Moreover, the phonon-frequency dispersion and q dependence of the matrix elements $\gamma(q)$ wash out this oscillation, which may be the case for the angle-averaged photoemission.[8] In principle, to obtain a quantitative description of the experimental ARPES one should use phonon densities of states at different temperatures determined from tunneling and

neutron spectroscopy, and take into account the impurity scattering and surface effects. In our opinion there are not enough experimental data available to attack this problem, at least at present. Nevertheless, the main experimental features of ARPES such as the existence of quasiparticles with a Fermi surface and the broad asymmetric line shape are in line with the polaronic nature of the charge carriers in the high-T_c metal oxides which have been independently observed by photoabsorption and modulation studies.[13] This reinforces, by now, the ample evidence for the polaronic nature of charge carriers manifest in a number of experiments such as photoinduced absorption,[13] optical conductivity,[14] XAFS measurements on local structural fluctuations,[15] etc. (for a recent review on this subject see for instance Refs. 16 and 17).

Finally, a very delicate and important question concerns the width of the coherent quasiparticle peak in the ARPES spectra. Experimentally it appears that this peak varies linearly with $|\varepsilon_{\mathbf{k}}-\varepsilon_F|$ where $\varepsilon_{\mathbf{k}}$ denotes the energy of the "quasiparticle." The theory developed in this paper cannot answer this question. It would require going beyond the mean-field decoupling equation (6) of the coherent polaronic motion and the incoherent background. In order to obtain lifetime effects of the small polarons, the scattering of small polarons by the excitations of the incoherent part of the spectrum would have to be included. This is planned for some future work.

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