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Theory of charge transfer at the high-T_c superconductor/electrolyte interface

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We discuss the kinetics of electrochemical process on the high-T_c superconducting electrodes dependent on the type of superconductivity. The existence of the hump of an appreciable height in the temperature dependence of the current clearly points towards the BCS s-type superconductivity, involving a gap in the electronic spectrum. The height of the hump should be much less in the case of the unconventional d-wave pairing, while the absence of the hump is a signal about the importance of pair-breaking processes typical of the strong-coupling theories or even about bipolaron (bosonic) mechanism. Low-temperature tails at the current/temperature curve are also informative being determined by the electronic states within the gap typical of the unconventional d-wave pairing.

The superconductors are attractive materials for applications as the electrodes in electrochemical systems. However, the study of their electrochemical properties began only recently after the discovery of the high-T_c superconductors (HTS). Extensive experimental investigations of the kinetics of the electronic transfer reactions were performed in a broad temperature region including the point of the superconducting transition T_c.[1–3] In most of the experiments the superconductors of the type $YBa_2Cu_3O_{7-\delta}$ were used in contact with solid electrolyte $Ag\beta'$—alumina. Rather common observation in various systems is a hump of the electric current near T_c. The increase of the current at the maximum point does not usually exceed a factor of 2 or 3.

The first theory of elementary electron transfer processes at the superconductor/electrolyte interface was presented in Refs. 4 and 5, where a quantum mechanical theory of the elementary act of charge transfer was extended to the systems under consideration. The traditional BCS model of the conventional weak-coupling superconductor was used in both papers. A qualitative explanation of the hump in the current/temperature derent/temperature dependence has been given in Ref. 6 based on the assumption of weak coupling of the reacting ions in the electrolytes with vibrational medium modes. This approach may serve as a basis for the extension of the theory to HTS, which is the aim of the present paper.

We assume below that the coupling of the electron acceptor (or donor) in the electrolyte with the electrode is small (nonadiabatic reaction). Then the electric current can be calculated using the theory of electrochemical electron transfer reactions developed in Refs. 7 and 8. The total electric current is the difference of anodic i_a and cathodic i_c currents related with the electron transitions from the reactant in the electrolyte to the electrode or in the opposite direction, respectively, $i = i_a - i_c$. The expressions for i_a and i_c have the form

$$i_a = \Phi_a e \int dE \rho(E)(1 - f(E))W_a(E), \qquad (1)$$

$$i_c = \Phi_c e \int dE \rho((E) f(E))W_c(E), \qquad (2)$$

where Φ_a and Φ_c are the functions of the reactant concentrations in the reaction zone, $\rho(E)$ and $f(E)$ are the DOS and Fermi distribution function for the electrons in the electrode, $W_a(E)$ and $W_c(E)$ are the probabilities (per unit time) of the electron transition to (or from) the electron energy level E in the electrode from (or to) the ion in the electrolyte. The electron energy is counted from the Fermi level.

The BCS theory of superconductivity based on the conventional s pairing in the weak-coupling limit implies the existence of an energy gap 2Δ near the Fermi level in the superconducting state and gives for the density of electronic states (DOS) outside the gap the following expression:

$$\rho(E) = \rho_0(E)\frac{|E|}{\sqrt{E^2 - \Delta^2}}, \qquad |E| > \Delta, \qquad (3)$$

where $\rho_0(E)$ is the DOS in the normal state, assumed to be a smooth function of E. Hereafter we put $\rho_0(E) = 1$. Δ may be approximately described by

$$\Delta = \Delta_0(1 - T/T_c)^{1/2}. \qquad (4)$$

Experimental data for HTS show that in some of them (e.g., in $Nd_{2-x}Ce_xCuO_4$ and in the newly discovered Hg based cuprates) a significant energy gap exists[9] with large values of the ratio $\frac{2\Delta_0}{T_c} = 5$–8. Experimental data are fitted better when a weak inelastic smearing (pair-breaking effects) is introduced to (3) following Dynes *et al.*:[10]

$$\rho_\Gamma(E) = \mathrm{Re}(\rho(E - i\Gamma)), \qquad (5)$$

where Γ is the lifetime broadening of the gap. Coffey proposed[11] for Γ the following temperature dependence:

$$\Gamma = \Gamma_0 + \Gamma_1(T/T_c)^3, \qquad (6)$$

where Γ_0 and Γ_1 are constants.

The deviations of the electronic properties from those of the conventional BCS with s pairing is even greater for HTS $YBa_2Cu_3O_{7-\delta}$ where the electronic states within the energy "gap" were found experimentally.[9] The DOS inside the "gap" depends on E linearly, while for $E \to \infty$ it behaves similarly to the conventional BCS, demonstrating also much weaker singularity (or even absence of singularity) at $|E| = \Delta$. These features of the DOS are characteristic for an unconventional BCS d-wave pairing, but the comprehensive microscopic theory is still in progress. In order to have the DOS which rationalizes these well established experimental features of the "gapless" HTS and does not rely on any particular microscopic theory we introduce the following model DOS:

$$\rho_d(E) = a\frac{|E|}{\Delta}, \qquad a = \frac{175}{96}, \qquad |E| \le \Delta, \tag{7}$$

$$\rho_d(E) = 1 + b\left(\frac{\Delta}{E}\right)^2 + \frac{3}{8}\left(\frac{\Delta}{E}\right)^4 + \frac{5}{16}\left(\frac{\Delta}{E}\right)^6 + \frac{35}{128}\left(\frac{\Delta}{E}\right)^8, \qquad b = -\frac{53}{384}, \qquad |E| > \Delta, \tag{8}$$

where a, b are the parameters determined by the condition of the continuity of the DOS at the points $|E| = \Delta$ and from the integral condition on the DOS: $\int_0^\infty (\rho_d(E) - 1)dE = 0$, which means simply that $\int \rho(E)dE$ is conserved on going into the superconducting state. Thus $\rho_d(E)$ depends only implicitly on the number of terms in Eq. (8), which is obtained from the expansion of (3) at large E.

The form of transition probability in Eqs. (1) and (2) depends on the strength of the coupling of the charge with the medium modes,[4] which for polar media is mainly characterized by the solvent reorganization energy E_r,[12] $E_r = (1/8\pi)(1/\epsilon_\infty - 1/\epsilon_0) \int (\vec{D}_i - \vec{D}_f)^2 d^3x$, where ϵ_0 and ϵ_∞ are the static and optical dielectric constants, and $\vec{D}_i$ and $\vec{D}_f$ are the electrostatic inductions due to the charge distributions in the initial and final states. If the reorganization energy is sufficiently small, then the dependence of the transition probability of the electron with energy E is of the resonance form[13]

$$W(E) = \frac{2V^2}{\hbar} \frac{\lambda k_b T}{(E+\delta)^2 + (\lambda k_b T)^2}, \tag{9}$$

where V is the electronic matrix element, δ depends on the electrode potential and reactant concentrations and $\lambda = \frac{2E_r}{\hbar\Omega^{(m)}} \ll 1$, where $\Omega^{(m)}$ is the characteristic vibrational frequency of the medium. The case when the concentrations of the reactants and products are maintained constant and equal to each other is considered below for the sake of simplicity. Since an exact form of the potential drop due to the conduction (normal) electrons of the superconductor is not known, we consider here the "classical" model of superconductor with no potential drop inside it. It is assumed also that all the potential drop occurs in the compact part of the double layer near the electrode. The potential drop in the diffuse layer of the electrolyte is taken into account by analogy to the so-called ψ effect leading to the corrected Tafel plots, i.e., we study the dependence of the current on the potential drop between the superconducting electrode and the point of location of reactant in the electrolyte. As usual we assume that it is located at the boundary of the compact layer. The quantity δ is then simply $\delta = \phi_0 - \phi$, where ϕ_0 is an equilibrium value of the electrode potential at which the total current i equals zero. Equation (9) is equally valid both for the forward and backward electron transfer. Since the potential is counted from the equilibrium one, introduced from the condition of zero total current, the functions of the reactant concentrations in Eqs. (1) and (2) are equal to each other. Taking into account that for the anodic and cathodic current δ has a different sign and the DOS is an even function of E, one can see from Eqs. (1), (2), and (9) that $i_c(\phi - \phi_0) = i_a(\phi_0 - \phi)$. The cathodic current will be therefore considered below in detail. We shall discuss mainly the behavior of the current at $T \le T_c$ in the neighborhood of T_c, where the maximum of the current has been observed.[1] The cathodic current dominates at $\phi_0 - \phi > 0$, whereas at $\phi_0 - \phi < 0$ the anodic current prevails.

The results for $\frac{i_c(T)}{i_c(T_c)}$ vs $\frac{T_c}{T}$ calculated for two different DOS [$\rho(E)$ and $\rho_d(E)$] are shown in Fig. 1. The height of the maximum is less for the "gapless" DOS and the behavior at $T \ll T_c$ is markedly different. An exponential

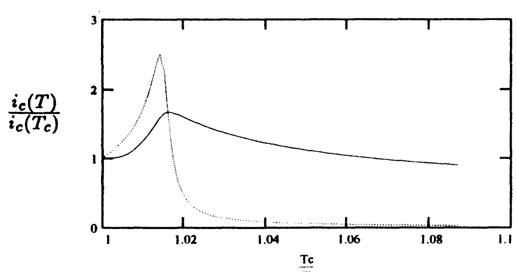

FIG. 1. Cathodic current $\frac{i_c(T)}{i_c(T_c)}$ vs $\frac{T_c}{T}$ calculated for two different DOS: $\rho(E)$ (dotted) and $\rho_d(E)$ (solid). Parameters: $k_b = 1; T_c = 100; \frac{\Delta_0}{T_c} = 4; \frac{\Gamma_0}{T_c} = 0.01; \Gamma_1 = 0; \lambda T_c = 2; \frac{\delta}{T_c} = 0.5$.

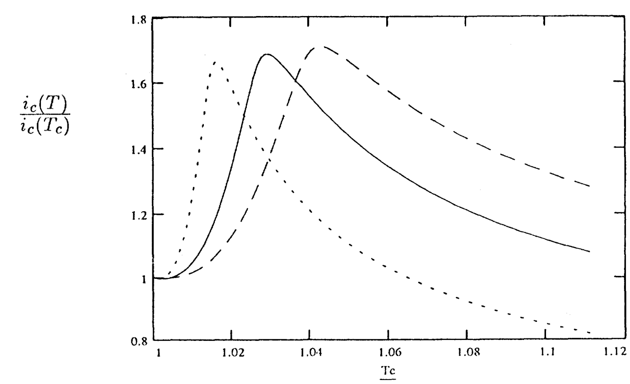

FIG. 2. Normalized cathodic current $\frac{i_c(T)}{i_c(T_c)}$ vs $\frac{T_c}{T}$ for the DOS given by $\rho_d(E)$ is shown for the three different ratios of $\frac{\Delta}{T_c}$: $\frac{\Delta}{T_c} = 4$ (dotted line); $\frac{\Delta}{T_c} = 3$ (solid line); $\frac{\Delta}{T_c} = 2.5$ (dashed line). Parameters: $k_b = 1$; $T_c = 100$; $\lambda T_c = 2$; $\frac{\delta}{T_c} = 0.5$.

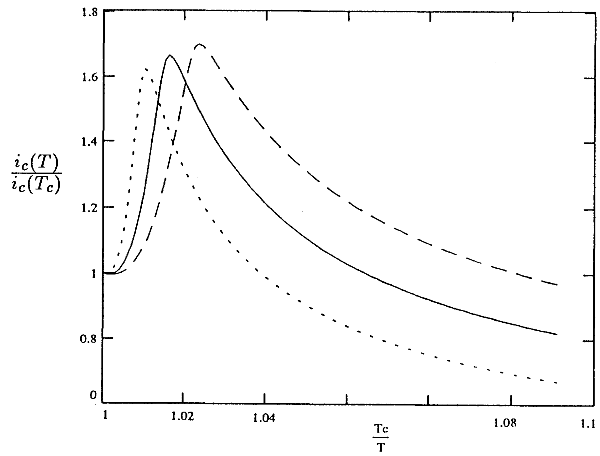

FIG. 3. Normalized cathodic current $\frac{i_c(T)}{i_c(T_c)}$ vs $\frac{T_c}{T}$ for the DOS given by $\rho_d(E)$ is shown for the three different values of the overpotential δ: $\frac{\delta}{T_c} = 0.4$ (dotted); $\frac{\delta}{T_c} = 0.5$ (solid); $\frac{\delta}{T_c} = 0.6$ (dashed). Parameters: $k_b = 1$; $T_c = 100$; $\frac{\Delta_0}{T_c} = 4$; $\lambda T_c = 2$.

decay typical of "gapped" BCS is replaced by the slow algebraic decay typical of the unconventional "gapless" theories. With growing ratio $\frac{2\Delta_0}{T_c}$ the maximum is shifted closer to T_c (see Fig. 2) while the height of the maximum remains almost unaltered. Increasing δ one can change both the position and height of the maximum (see Fig. 3).

The results presented above should be supplemented with the discussion of the pair-breaking processes, which play an important part in the numerous explanations of the NMR phenomena in HTS. Calculations with the DOS $\rho_\Gamma(E)$ (5) and Γ given by (6) demonstrate that already for rather weak intensity of the pair-breaking processes $\frac{\Gamma_0}{\Delta_0} = 0.1$ the hump of the current is fully suppressed (see Fig. 4). This might be the reason why the hump was not reliably detected in the experiments of Ref. 3 with Tl-based HTS.

Another model of superconductivity, based on bipolaronic mechanism, considers the elementary excitations in the superconductor as the charged weakly imperfect quasi-two-dimensional Bose gas with temperature dependent plasmon gap Ω in the elementary excitations spectrum,[14]

$$E = \sqrt{\frac{k^4}{4m^2} + \frac{k^2}{2m} n\, v(k) + \Omega^2}, \tag{10}$$

where $v(k) = \frac{1}{k}$ is the correction to the spectrum of neutral bosons taking into account the charge of the particles. The superfluid density $n(T)$ involved in (10) is assumed to be described in the form proposed in Ref. 15: $n(T) = n_0(1 - T/T_c)^{2/3}$, which takes into account critical fluctuations close to the temperature T_c of the transition from the superfluid to normal state. The Fermi function in Eq. (2) must be changed now to the Bose function and the integration performed directly in k space where the properties of the system are determined by the elementary excitations spectrum. The results are shown in Fig. 5. The temperature dependence of $\frac{i_c(T)}{i_c(T_c)}$ has no peaks. This feature may serve for discrimination between the Bose and Fermi models of HTS.

Only cathodic current was considered above. At negative overpotentials $\phi - \phi_0$ it dominates and is approximately equal to the total current. The dependence of the absolute value of the total electric current $|i|$ on δ is very informative, because it follows qualitatively to the shape of the DOS. The current/voltage dependencies for

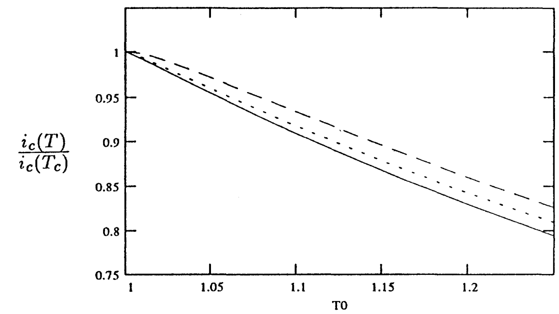

FIG. 5. The temperature dependence of $\frac{i_c(T)}{i_c(T_c)}$ calculated for the bipolaronic model with the elementary excitations spectrum given by Eq. (10) for the three different values of δ: $\delta = 1$ (solid); $\delta = 0.7$ (dotted); $\delta = 0.25$ (dashed). Parameters: $k_b = 1$, $T_c = 5$, $\Omega = 0.05$, $m = 10$, $n_0 = 1$.

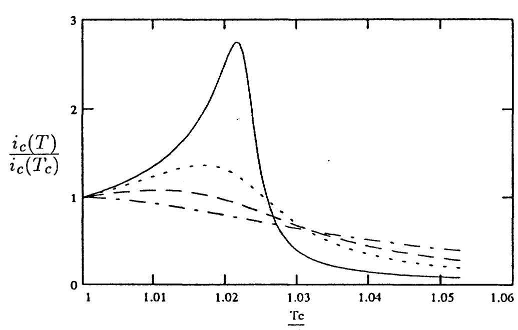

FIG. 4. Normalized cathodic current $\frac{i_c(T)}{i_c(T_c)}$ vs $\frac{T_c}{T}$ calculated with the DOS $\rho_\Gamma(E)$ and Γ given by Eq. (6) for the four different values of Γ: $\Gamma_0 = 1$, $\Gamma_1 = 0$ (solid); $\Gamma_0 = 10$, $\Gamma_1 = 0.5$ (dotted); $\Gamma_0 = 20$, $\Gamma_1 = 1$ (dashed); $\Gamma_0 = 40$, $\Gamma_1 = 2$ (dashed-dotted). Parameters: $k_b = 1$; $T_c = 100$; $\frac{\Delta_0}{T_c} = 4$; $\lambda T_c = 2$; $\frac{\delta}{T_c} = 0.5$.

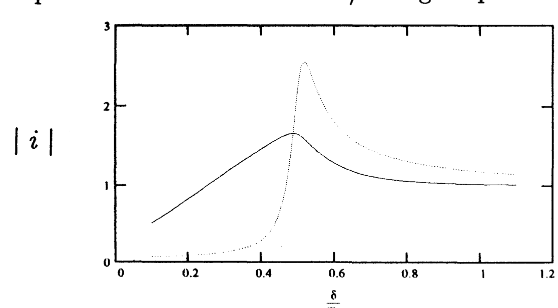

FIG. 6. The dependence of the absolute value of the normalized total electric current $|i|$ on the overpotential δ for the "gapped" $\rho(E)$ (dotted) and "gapless" $\rho_d(E)$ (solid). Parameters $k_b = 1$; $T_c = 100$; $T = 98.5$; $\frac{\Delta_0}{T_c} = 4$; $\frac{\Gamma_0}{T_c} = 0.01$; $\Gamma_1 = 0$; $\lambda T_c = 2$.

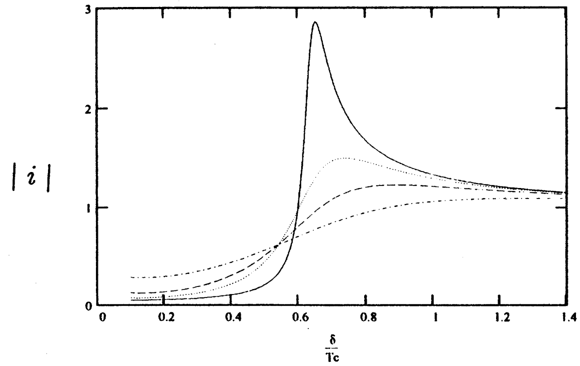

FIG. 7. Absolute value of the normalized total electric current $|i|$ vs overpotential δ, calculated with the DOS $\rho_\Gamma(E)$ and Γ given by Eq. (6) for the four different values of Γ: $\Gamma_0 = 1$, $\Gamma_1 = 0$ (solid); $\Gamma_0 = 10$, $\Gamma_1 = 0.5$ (dotted); $\Gamma_0 = 20$, $\Gamma_1 = 1$ (dashed); $\Gamma_0 = 40$, $\Gamma_1 = 2$ (dashed-dotted). Parameters: $k_b = 1$; $T_c = 100$; $T = 97.5$; $\frac{\Delta_0}{T_c} = 4$; $\lambda T_c = 2$.

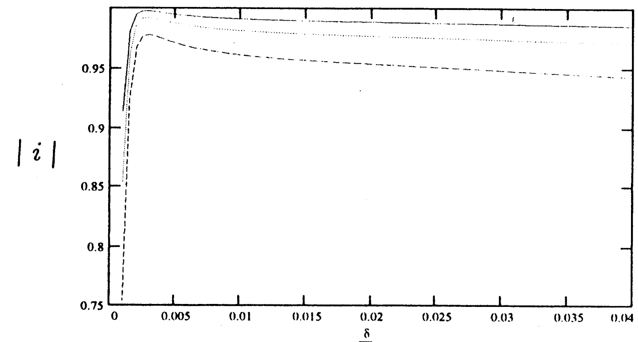

FIG. 8. Total electric current $|i|$ (normalized to its value at $T = T_c$) vs overpotential δ, for the bipolaronic model with the energy spectrum given by Eq. (10) for the three different temperatures: $T = 4.95$ (solid); $T = 4.9$ (dotted); $T = 4.8$ (dashed). Parameters: $k_b = 1$, $T_c = 5$, $\Omega = 0.05$, $m = 10$, $n_0 = 1$.

the "gapped " $\rho(E)$ and "gapless" $\rho_d(E)$ are compared in Fig. 6 and manifest a significant difference originating from the peculiar features of the unconventional d-wave pairing. The height of the hump is much less in the case of the unconventional d-wave pairing and the tail of the current under low values of δ is seen at the current and/or overpotential curve, being determined by the electronic states within the gap typical of the unconventional d-wave pairing.

The effect of pair-breaking phenomena on the system with s-type pairing and DOS given by $\rho_\Gamma(E)$ is also considerable. Already at moderate $\frac{\Gamma_0}{\Delta_0} = 0.1$ the peak due to the electronic states at the edge of the gap is smeared out (see Fig. 7). For the bipolaronic model the peak is always absent and even at the maximum the current is suppressed as compared to its value at T_c (see Fig. 8).

Thus the kinetics of electrochemical process on superconducting electrodes depend on the type of superconductivity and may serve as an additional tool for discrimination between the different models. The possibility of getting information both from the temperature and potential dependencies of the current is notable.

It is worthwhile to point out that all the results presented above are obtained for the values of parameters typical of the high-T_c superconductors and of the electrochemical experiment; therefore, changing the values of parameters does not change considerably the appearance of the plots and at the present stage one can distinguish between the models at the qualitative level. The existence of the hump of an appreciable height (the increase of the current by a factor of 2 or 3) in the temperature dependence of current clearly points towards the weak-coupling BCS scheme of superconductivity with s-wave pairing. The height of the hump should be much less in the case of the unconventional d-wave pairing, while its absence is a signal about the importance of pair-breaking processes typical of the strong-coupling theories or even about bipolaron (bosonic) mechanism. Low-temperature tails are also very informative being related to the electronic states within the gap and supplying information about the shape of DOS in this region. The exponential tail is typical of the weak-coupling BCS scheme with s pairing, while the unconventional d pairing will show up in the algebraic tail.

More experimental data for different gapped and gapless superconductors, especially on the current vs potential curves, are needed to make any solid conclusion about the peculiarities of the quantum electrochemical processes in HTS and their relationship with the electronic structure of these materials.

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