Polaron theory of high-temperature superconductors

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It is shown that a systematic theory of strong electron-phonon interaction that takes account of the formation of small polarons and bipolarons gives a satisfactory description of the basic properties of high-temperature metal-oxide superconductors.

The discovery of high-temperature superconductors (HTS)[1,2] has given a powerful impetus to the creation of a large number of new theories of high-temperature superconductivity. In this connection two very fundamental questions have arisen: First, what type of theory (mean-field theory (BCS), or a theory of local bipolaron pairs[3,4]) describes the new HTS's most adequately, and, second, what interaction (Coulomb[5] or electron-phonon) is responsible for the formation of the pairs?

In this paper we consider a broad spectrum of experimental data that appear to confirm the applicability of the many-polaron theory of superconductors with strong coupling[3,4] to the HTS's La–Ba–Cu–O, La–Sr–Cu–O, Y–Ba–Cu–O, and other metal oxides.

As noted earlier,[6] the condition for strong electron-phonon coupling

$$\lambda \geqslant 1 \tag{1}$$

practically coincides with the condition for the formation of a small-radius polaron

$$f(z)\, g^2\omega/D \geqslant 1, \tag{2}$$

fulfillment of which is accompanied by a substantial renormalization of the electron spectrum, expressed in an exponential narrowing of the original electron band, with width $2D$, to a very narrow polaron band, with half-width

$$W = D\exp(-g^2). \tag{3}$$

Here $f(z) = (2z)^{1/2}$, z is the coordination number of the lattice, and g^2 and ω are the dimensionless electron-phonon coupling constant and the characteristic frequency of the vibrations, respectively, determined by the usual Fröhlich Hamiltonian in the momentum representation or site representation:

$$H_{e-ph} = \sum_{\mathbf{qk}} [u(\mathbf{q})\, c^{+}_{\mathbf{k}+\mathbf{q}} c_{\mathbf{k}} d_{\mathbf{q}} + \text{H.c.}] = \sum_{\mathbf{qn}} [u(\mathbf{q})\, e^{i\mathbf{qn}} c_{\mathbf{n}}^{+} c_{\mathbf{n}} d_{\mathbf{q}} + \text{H.c.}],$$

$$g^2 = \sum_{\mathbf{q}} \omega_{\mathbf{q}}^{-2} \operatorname{cth}\left(\frac{\omega_{\mathbf{q}}}{2T}\right) u^2(\mathbf{q})\,(1-\cos \mathbf{qn}),$$

$$\omega \equiv g^{-2} \sum_{\mathbf{q}} \omega_{\mathbf{q}}^{-1} u^2(\mathbf{q}); \tag{4}$$

$c_{\mathbf{q}}$ and $d_{\mathbf{q}}$ are electron (hole) and phonon operators, respectively, $\omega_{\mathbf{q}}$ is the phonon frequency, and $\mathbf{n}$ is a translation vector of the lattice.

Thus, Migdal's well known theorem is violated in the strong-coupling limit (1) (Ref. 8). The system turns out to be in the nonadiabatic regime:

$$\varepsilon_F \lesssim W \lesssim \omega, \tag{5}$$

where ε_F is the unrenormalized Fermi energy.

As shown by the many-polaron theory, allowance for the polaron effect (3) qualitatively changes the nature of the superconducting state: In the intermediate region $\lambda \approx 1$ ordinary superconductivity of the BCS type gives way to polaron[4] and bipolaron superconductivity in the strong-coupling limit $\lambda \gg 1$ (Ref. 3).

For a polaron superconductor (PS) (Ref. 4),

$$T_c \approx 1.14 W (1-\varepsilon_F^2/W^2)^{1/2} \exp\left(-\frac{2W}{v_0 + z v_1 \varepsilon_F^2/W^2}\right), \tag{6}$$

where v_0 and v_1 are the single-site and intersite polaron-polaron interactions of order $g^2\omega$, due to the local deformation of the lattice.

For a bipolaron superconductor (BS) (Refs. 3, 6, 9),

$$T_c = f(p)/m^{**}. \tag{7}$$

Here $f(p)$ is a function of the carrier concentration p: $f(p) \approx 3.3p^{2/3}$ for small values of p; m^{**} is the effective bipolaron mass:

$$m/m^{**} = 2T_{nn'}^2 \Delta^{-1} \exp(2g^2) \int_0^\infty d\tau \exp[-2g^2 \exp(\omega\tau/\Delta) - \tau], \tag{8}$$

where $T_{nn'} \sim D$ is the initial hopping integral, m is the band mass in the rigid lattice, $\Delta \approx 2g^2\omega - V_c$ is the binding energy of the bipolaron, and V_c is the Coulomb repulsion of polarons at the same site or neighboring sites (depending on whether single-site or two-site bipolarons are formed).

As a result, instead of the monotonic decrease of $T_c \propto \lambda^{1/2}$ with increase of the electron-phonon interaction, predicted by the theory of Éliashberg, the polaron theory of superconductivity predicts a rather narrow maximum T_c^* in the dependence $T_c(\lambda)$ (Fig. 1). One can estimate T_c^* with the aid of Eqs. (6) and (2):

$$T_c^* \approx 0.5\omega. \tag{9}$$

Thus, in the case of interaction with the high-frequency oxygen vibrational mode onecan obtain $T_c^* \approx 500$ K.

We shall consider the basic properties of HTS, taking into account the circumstance that a BS is similar to superfluid ^{4}He (Ref. 3).

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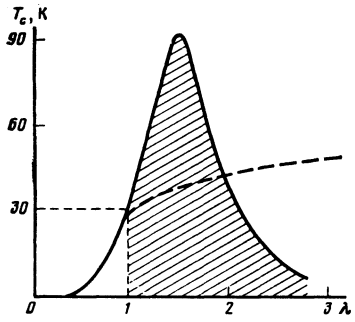

FIG. 1.

1. HIGH T_c

Using Eq. (7) with realistic values of $g^2 \approx 2$, $T_{nn'}$, Δ, and $\omega \sim 0.1$ eV, we can estimate

$$m^{**} \approx (50-100)\, m, \tag{10}$$

which gives $T_c \gtrsim 100$ K for $p \approx (0.5\text{–}1) \cdot 10^{22}$ cm^{-3} (Hall measurements).

2. THE LONDON PENETRATION DEPTH $\lambda_H(T)$

With the same values of m^{**} and p we obtain a huge depth of penetration of a magnetic field:

$$\lambda_H(0) = \left(\frac{m^{**}}{8\pi p e^2}\right)^{1/2} \gtrsim 3000 \text{ Å}, \tag{11}$$

which agrees with muon-spin relaxation data.[11]

For a charged Bose gas the dependence $\lambda_H(T)$ is described by the equation

$$\lambda_H(T) = \lambda_H(0)\left(1 + \frac{1}{3pm}\int \frac{d^3p}{(2\pi)^3}\, \mathbf{p}^2 \frac{\partial f}{\partial \varepsilon}\right)^{-1/2}, \tag{12}$$

where $f(\varepsilon)$ is the Bose distribution function.

Using the excitation spectrum $\varepsilon(p)$ for a BS (Ref. 3), we can obtain a power dependence $\lambda_H(T)$ for $T \ll T_c$:

$$\lambda_H(T) \approx \lambda_H(0)\,[1+(T/T_c)^{\alpha}], \tag{13}$$

where $3/2 < \alpha \leqslant 4$, which is characteristic of "1–2–3" compounds.

3. THE UPPER CRITICAL FIELD $H_{c2}(T)$

Small bipolarons are heavy interacting charged bosons. The upper critical field of a charged Bose gas has the form

$$H_{c2}(T) = H_{c1}(1-t^{3/2})^{1/2}/t \tag{14}$$

in the "clean" limit,[12] and

$$H_{c2}(T) = H_d(1-t^{3/2})^{1/2}/t^{3/2} \tag{15}$$

in the "dirty" limit.[6] Here

$$H_{c1} = 0.18\phi_0 m^{**} T_c \eta^{1/2},$$
$$H_d = 0.24\phi_0 l^{-1/2}(m^{**}T_c)^{1/2}$$

are temperature-independent constants determined by the mean free path of the bosons, $\phi_0 = \pi/e$, η is the gas parameter for a weakly interacting Bose gas, and l is the mean free path for scattering by impurities.

Equations (14) and (15) both predict nonlinear behavior of H_{c2} near T_c:

$$H_{c2} \propto (T_c - T)^{1/2},$$

which agrees well with the experimental data for $YBa_2Cu_3O_{7-x}$ single crystals in a wide range of temperatures.[13]

4. THE SPECIFIC HEAT

The first experiments[14] gave a rather low value of the Sommerfeld constant in the normal phase:

$$\gamma \leqslant 5 \text{ mJ/mole}\cdot\text{K}^2. \tag{16}$$

It is now clear[15] that the low value (16) of γ was due to an error in the determination of the slope $[dH_{c2}(T)/dT]_{T_c}$ as a consequence of the nonlinear dependence $H_{c2}(T)$, and to an overestimated value of the resistivity ρ in the first ceramic samples.

It has been found that the new HTS have a large value of γ (Refs. 15, 16):

$$\gamma \gtrsim 30 \text{ mJ/mole}\cdot\text{K}^2, \tag{17}$$

which is of the same order as (and even higher than) the value in A-15 superconductors.

Taking into account that $\gamma \sim p^{1/3} m^{**}$ (Ref. 6) and $\lambda_H \sim p^{-1/2}(m^{**})^{1/2}$, and using (11) and (17), we obtain

$$m^{**} \gtrsim 20m, \quad p \leqslant 10^{22} \text{ cm}^{-3}, \tag{18}$$

which agrees with the estimate (10) and with the Hall measurements.

One of the most surprising properties of the new HTS is the huge discontinuity of the specific heat in single crystals at $T = T_c$ (Ref. 17). The specific heat per carrier is

$$\Delta C/p \gtrsim 0.5 k_B \tag{19}$$

where k_B is the Boltzmann constant. The value (19) is evidence that all the carriers take part in the formation of the condensate (as in liquid ^{4}He), and not just a small fraction of them (as follows from BCS theory). Near T_c the $C(T)$ dependence should be as in ^{4}He, and this, apparently, is observed in "1–2–3" compounds.[18]

5. THE ISOTOPE EFFECT

The first measurements gave the value

$$\alpha = -d\ln T_c / d\ln M < 0.2, \tag{20}$$

where m is the mass of the oxygen atom. In the framework of BCS theory the rather low value (20) of α can be explained by the anharmonicity of the oxygen modes, and also by Coulomb effects.

The polaron theory gives a zero isotope effect at the maximum of the curve $T_c(\lambda)$ (Fig. 1). On the other hand, bipolaron limit ($\lambda \gg 1$) one can obtain a huge isotope effect $\alpha > 0.5$ by assuming that high-frequency modes with $\omega \sim M^{-1/2}$ give the main contribution to g^2 (4).

In this case, using (7) and taking (8) into account, we obtain

$$\alpha = g^2 F(\Delta/\omega, g^2), \tag{21}$$

where

$$F(x,y) = 1 + M^{-1}(1, 1+x, y)\left[M(1, 2+x, y) - \frac{x}{y}\frac{dM(1, 1+x, y)}{dx}\right]$$

is a smooth function varying from $F(\infty, y) = 2$ to $F(0,y) = 1$, and $M(a,c,z)$ is a confluent hypergeometric function.

Thus, $g^2 \approx 2$ gives $\alpha > 2$, and this explains the surprising result from the Los Alamos laboratory.[19]

6. THE X-RAY-EMISSION SPECTRA AND THE SPECTRA OF INELASTIC ELECTRON SCATTERING

These spectra make it possible to suggest that HTS based on cuprates have an energy structure (Fig. 2) in which the O $2p$ band lies in the Coulomb gap $U >$ eV between two Cu $3d$ Hubbard sub-bands. It is in this rather narrow O $2p$ band that the small polarons and bipolarons are formed.

To summarize, one can give an answer to the most important questions:

1) The metal-oxide HTS such as LBCO, LSCO, YBCO, Bi-Sr-Ca-Cu-O, Tl-Ba-Ca-Cu-O, $SrTiO_3$, Ba-Pb-Bi-O, $LiTiO_2$, K-Ba-Bi-O, etc. are bipolaron superconductors that can be described by the polaron theory of superconductivity.[3,4]

2) The measured isotope effect (20), tunneling spectroscopy, band calculations, and certain other experiments provide evidence in favor of an electron-phonon mechanism of the interaction in HTS. In conclusion, we note that the polaron theory of HTS explains the high values of T_c exclusively as the result of an appropriate combination of the initial electron bandwidth D and the electron-phonon coupling constant g^2 (Fig. 1). Therefore, neither the complex structure nor the presence of copper is very important for the high values of T_c.

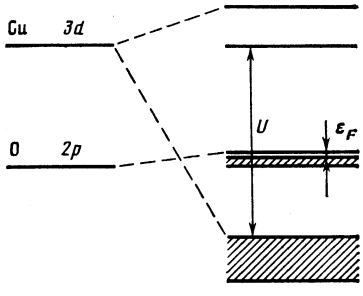

FIG. 2.

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