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New theory of strong-coupling superconductors and high-temperature superconductivity of metallic oxides

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An explanation of some of the anomalous properties of La-Ba-Cu-O, La-Sr-Cu-O, and Y-Ba-Cu-O superconductors on the basis of the small bipolaron theory of Alexandrov and co-workers is proposed.

Tunnel spectroscopy, heat measurements, and band-structure calculations favor a strong electron-phonon coupling in the new metallic oxide superconductors. However, the traditional theory of electron-phonon interaction in metals hardly explains high values of $T_c \sim 100$ K.

On the other hand, it is well known[1] that in *d*- and *f*-bands metallic oxides with sufficiently narrow electronic bands $-D \lesssim 1$ eV (D is a half-bandwidth) the polaron narrowing of the band and corresponding mass enhancement occur:

$$W = D\exp(-g^2),\ m^*/m = \exp(g^2)\ . \tag{1}$$

The traditional theory of metals and superconductors does not take into account the polaron narrowing of the band Eq. (1). But the many-polaron theory shows that the taking into account of the polaron effects qualitatively changes the nature of the superconducting state: In the intermediate coupling region $\lambda \simeq 1$ the ordinary Bardeen-Cooper-Schrieffer (BCS) superconductivity is replaced by polaron[2] and bipolaron superconductivity in the strong coupling limit $\lambda \gg 1$.[3] Here $g^2 = \lambda D/2z\omega$, ω is a characteristic phonon frequency, and z is the nearest neighbor's number.

In the polaron superconductors the Cooper pairs are formed by small polarons. The critical temperature of a polaronic superconductor is much greater than the BCS value as a consequence of the polaron enhancement Eq. (1) of the electron density of states:[2]

$$T_c = 1.14W(1-\varepsilon_F^2/W^2)^{1/2}\exp\left[-\frac{2W}{v_0 + Zv_1\varepsilon_F^2/W^2}\right]\ , \tag{2}$$

where v_0, v_1 are the on-site and the intersite effective polaron-polaron interaction correspondingly, ε_F is the Fermi level in relation to the middle of the band.

In the case of bipolaron superconductors ($\lambda \gg 1$) the localized real-space pairs are formed at ambient or high temperatures which are influenced by superfluid transitions as in liquid helium at the critical temperature:[3]

$$T_c \simeq 3.3(n/2)^{2/3}/m^{**}\ , \tag{3}$$

where n is the electron concentration and m^{**} is a bipolaron effective mass, $m^{**} \gtrsim m^*\Delta/W$, Δ is a bipolaron binding energy.[3]

As a result, instead of a monotonous rise of T_c with the increase of the constant of the electron-phonon coupling, predicted by the BCS theory and generalized for the case of strong coupling, the many-polaron theory predicts a rather narrow maximum of the dependence of $T_c(\lambda)$ (Fig. 1).

Notably, the T_c maximum is considerably higher than that predicted by the BCS theory ($\lesssim 30$ K) resulting from the polaron effect, which causes an enormously high electron density of states.

Assuming $m^{**} = 100m_e$, $\frac{1}{2}n = 10^{22}$ cm^{-3}, and using Eq. (3), we have $T_c \simeq 130$ K.

As we previously mentioned[4] (see also Refs. 1 and 5), the new high-temperature superconductors La-Ba-Cu-O, La-Sr-Cu-O, Y-Ba-Cu-O, and others could be bipolaronic by nature.

Here we propose a qualitative explanation of some of their properties based on the assumption of the strong electron-phonon interaction and on our theory of bipolarons.[2,3]

The high resistivity in the normal state $\rho \sim 100\ \mu\Omega$ cm with the carriers density $n \simeq 10^{22}$ cm^{-3} indicates a low

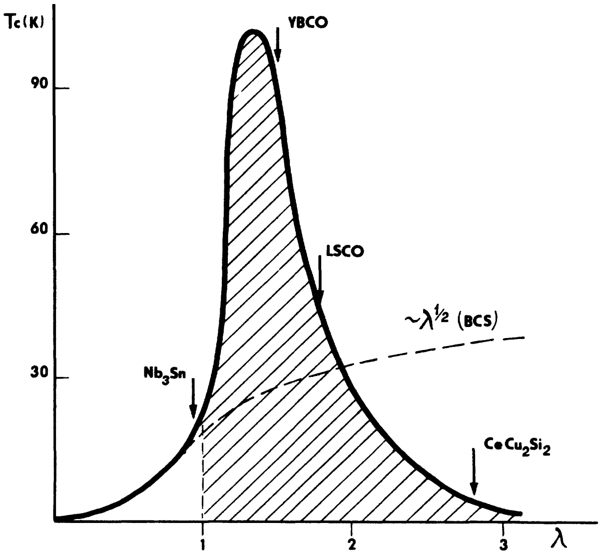

FIG. 1. Dependence of the critical temperature on the electron-phonon coupling constant. The shading shows the area of polaron and bipolaron superconductivity. The dotted line corresponds to the BCS theory, generalized for the strong coupling case.

mobility which could be a consequence of polaron mass enhancement [Eq. (1)].

Soft phonon modes make the main contribution to the electron-phonon constant g^2.[13] This fact explains the linear dependence of $\rho(T)$.

The high value of the thermoelectric power at a sufficiently low temperature [$\alpha = 20\ \mu\text{V/K}$, $T = 40$ K La-Ba-Cu-O (Ref. 6)] indicates a low value of the characteristic kinetic energy of the carriers and gives

$$m^*/m_e \gtrsim 20\ . \tag{4}$$

Low-temperature measurements of the heat capacity[7] gives an enormously high value of γ, which exceeds the values for $A15$ compounds, and sufficiently low Debye temperature Θ_D:

$$\begin{aligned} &\mathrm{La_{1.8}Sr_{0.2}CuO_4}\text{: } \gamma = 39\ \text{mJ/mol}\,\text{K}^2,\ \Theta_D = 186\ \text{K}\ , \\ &\mathrm{La_{1.85}Ba_{0.15}CuO_4}\text{: } \gamma = 71\ \text{mJ/mol}\,\text{K}^2,\ \Theta_D = 188\ \text{K}\ . \end{aligned} \tag{5}$$

It must be mentioned that the first estimations of $\gamma \simeq 6$ mJ/mol K^2 (Ref. 8) based on the temperature dependence of the upper critical field and on the value of residual resistivity seem to be insufficient because of the nonlinear $H_{c2}(T)$ dependence near T_c and the great error in the determination of the value of ρ.

At present we have the muon-spin-relaxation measurements of magnetic-field penetration depth on $\mathrm{La_{1.85}Sr_{0.15}CuO_4}$ (Ref. 9):

$$\lambda_H = 2500\ \text{Å}\ . \tag{6}$$

Taking into account that $\gamma \sim m^* n^{1/3}$ and $\lambda_H \sim (m^*)^{1/2} n^{-1/2}$, one obtains [Eqs. (5) and (6)]

$$m^*/m_e \gtrsim 29,\ n \gtrsim 1.2\times 10^{22}\ \text{cm}^{-3}\ . \tag{7}$$

These values agree well with the assumption of the polaron mass enhancement Eq. (1) and with the Hall effect measurements.

As was shown in Ref. 10, the anomalous pressure dependence $T_c(p)$ of the lanthanium and yttrium ceramics rules out the BCS as well as Anderson's resonating valence bond (RVB)[11] models, but can be explained in the framework of bipolaronic superconductivity.[3]

We have mentioned[4] that the temperature dependences of the magnetic susceptibility suggest that lanthanium ceramics are bipolaronic superconductors with $\lambda \gtrsim 2$ while yttrium ones are polaronic with $\lambda \simeq 1$.

Using Eqs. (2) and (3) one can obtain a great value of dT_c/dp easily for bilpolaronic superconductors[10] and a much lower value for polaronic ones [Eq. (3)].

Since the soft modes make the main contribution to g^2 (Ref. 3), the isotope effect could be negligibly small in the polaronic case [Eq. (2)] and greater but rather small in the bipolaronic one [Eq. (3)].

Near the maximum on the curve of the dependence of $T_c(\lambda)$ (Fig. 1) the isotope effect tends to zero.

As was mentioned by Mott[1] the observation of the Anderson localization effects, which is unlikely unless the effective mass of the carriers is enhanced, a layer structure, as well as mixed valence states of Cu favor the bipolaron picture of the new high-temperature superconductors.

The main purpose of this paper is to show that the ordinary electron-phonon interaction can produce high T_c as a result of polaron narrowing of the band, which is not considered by the traditional theory of strong-coupling superconductors, based on Migdal-Eliashberg equations. Even in the range of moderate values of $\lambda \simeq 1$ one is in the so-called antiadiabatic limit

$$\varepsilon_F \sim W \lesssim \omega\ , \tag{8}$$

so the traditional theory is inapplicable.

It is interesting to point out that according to the polaron theory of superconductivity[2-4,12] the substantial different values of T_c of various d- and f-band metallic compounds, like $A15$ ($\mathrm{Nb_3Sn}$,$\mathrm{V_3Si}$), "heavy-fermion" systems ($\mathrm{CeCu_2Si_2}$), and new superconducting lanthanium and yttrium cuprates are explained exclusively by the different values of bandwidth D and of electron-phonon coupling λ, resulting in the different values of the polaron (m^*) and bipolaron (m^{**}) effective masses. As an example, in $\mathrm{CeCu_2Si_2}$ the f-band is very narrow, so $m^{**} \gtrsim 1000\ m_e$. As a result, according to Eq. (3), $T_c < 10$ K (see also Fig. 1).

It seems that La-Sr-Cu-O and Y-Ba-Cu-O have intermediate values of D and λ and are in the vicinity of the maximum of $T_c(\lambda)$ (Fig. 1).

Near the maximum of $T_c(\lambda)$, $T_c \simeq W$, so ε_F is of the same order as T_c. Consequently, all the electrons of the polaronic superconductor participate in the formation of the Bose condensate. As a result, the value of the specific heat jump per one carrier $\Delta C/n$ for $T = T_c$ is of the order of the Bolzmann constant k_B.

According to Ref. 13 in Y-Ba-Cu-O

$$\Delta C \simeq 5\ \text{J/mol}\,\text{K}\ ,$$

so

$$\Delta C/nk_B \simeq 0.5\ . \tag{9}$$

It seems that the result [Eq. (9)] presents a direct proof of the polaronic nature of the new high-T_c superconductors.

In conclusion, we summarize our main results. (a) The polaronic effect leads to the substantial enhancement of T_c. (b) The polaronic enhancement of the mass of carriers explains the extraordinary high values of λ_H, γ, α, ρ, and dT_c/dp. (c) The anomalous value of $\Delta C/nk_B$ in La-Ba-Cu-O, La-Sr-Cu-O, and Y-Ba-Cu-O demonstrates the nonadiabatic character of the motion of carriers $\varepsilon_F \lesssim \omega$.

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