Superlight bipolarons and a checkerboard d-wave condensate in cuprates

A.S. Alexandrov

Department of Physics, Loughborough University, Loughborough LE11 3TU, UK

The seminal work by Bardeen, Cooper and Schrieffer taken further by Eliashberg to the intermediate coupling solved the problem of conventional superconductors about half a century ago. The Fröhlich and Jahn-Teller electron-phonon interactions were identified as an essential piece of physics in all novel superconductors. The BCS theory provides a qualitatively correct description of some of them like magnesium diborade and doped fullerenes (if the polaron formation is taken into account). However, cuprates remain a problem. Here I show that the bipolaron extension of the BCS theory to the strong-coupling regime could be a solution. Low-energy physics in this regime is that of small ‘superlight’ bipolarons, which are real-space mobile bosonic pairs dressed by phonons. The symmetry and space modulations of the order parameter are explained in the framework of the bipolaron theory. A d-wave Bose-Einstein condensate of bipolarons reveals itself as a checkerboard modulation of the hole density and of the gap below $T_c$.

PACS numbers: PACS: 74.72.-h, 74.20.Mn, 74.20.Rp, 74.25.Dw

I. INTRODUCTION: PAIRING IS INDIVIDUAL IN MANY CUPRATES

Experimental [1, 2, 3, 4, 5, 6, 7, 8] and theoretical [9, 10, 11, 12, 13] evidence for an exceptionally strong electron-phonon interaction in high temperature superconductors is now so overwhelming, that even some advocates of nonphononic mechanisms [14] accept this fact. Our view is that the extension of the BCS theory towards the strong interaction between electrons and ion vibrations describes the phenomenon naturally. High-temperature superconductivity exists in the crossover region of the electron-phonon interaction strength from the BCS-like to bipolaronic superconductivity as was predicted before [15], and explored in greater detail after the discovery [10, 16, 17, 18, 19, 20, 21].

Polarons form the Cooper pairs, if their coupling is not strong enough. However, real-space small bipolarons are also feasible due to a polaron collapse of the Fermi energy. There is strong evidence for the Bose-Einstein condensation of small bipolarons in many cuprates, in particular at low doping. Let us, for example, estimate a renormalised Fermi energy. The band structure is quasi-two-dimensional with a few degenerate hole pockets in cuprates. Applying the parabolic approximation for the band dispersion we obtain the renormalized Fermi energy as

$$\epsilon_F = \frac{\pi n_i d}{m_i^*},$$

where $d$ is the interplane distance, and $n_i, m_i^*$ are the density of holes and their effective mass in each of the hole subbands $i$ renormalized by the electron-phonon (and by any other) interaction. One can express the renormalized band-structure parameters through the in-plane magnetic-field penetration depth at $T \approx 0$, measured experimentally:

$$\lambda_H^{-2} = 4\pi\epsilon^2 \sum_i \frac{n_i}{m_i^*}.$$  (2)

As a result, we obtain a parameter-free expression for the “true” Fermi energy as

$$\epsilon_F = \frac{d}{4\pi e^2 \lambda_H^2},$$  (3)

where $g$ is the degeneracy of the spectrum, which may depend on doping. One expects 4 hole pockets inside the Brillouin zone (BZ) due to the Mott-Hubbard gap in underdoped cuprates. If the hole band minima are shifted with doping to BZ boundaries, all their wave vectors would belong to the stars with two or more prongs. The groups of wave vectors for these stars have only 1D representations. It means that the spectrum will be degenerate with respect to the number of prongs, i.e $g \geq 2$. Because Eq.(3) does not contain any other band-structure parameters, the estimate of $\epsilon_F$ using this equation does not depend very much on the parabolic approximation for the band dispersion.

Generally, the ratios $n/m^*$ in Eq.(1) and Eq.(2) are not necessarily the same. The ‘superfluid’ density in Eq.(2) might be different from the total density of delocalized carriers in Eq.(1). However, in a translationally invariant system they must be the same [22]. This is also true even in the extreme case of a pure two-dimensional superfluid, where quantum fluctuations are important. One can, however, obtain a reduced value of the zero temperature superfluid density in the dirty limit, $l \ll \xi(0)$, where $\xi(0)$ is the zero-temperature coherence length. The latter was measured directly in cuprates as the size of the vortex core. It is about $10 \, \AA$ or even less. On the contrary, the mean free path was found surprisingly large at low temperatures, $l \sim 100-1000 \, \AA$. Hence, it is rather probable that novel superconductors are in the clean limit,
TABLE I: The Fermi energy (multiplied by the degeneracy) of cuprates

| Compound          | $T_c$ (K) | $\lambda_{H,ab}$ (Å) | $d(\bar{A})$ | $\epsilon_F$ (meV) |
|-------------------|-----------|-----------------------|---------------|-------------------|
| La$_{1.8}$Sr$_{0.2}$CuO$_4$ | 36.2      | 2000                  | 6.6           | 112               |
| La$_{1.76}$Sr$_{0.24}$CuO$_4$ | 27.5      | 1980                  | 6.6           | 114               |
| La$_{1.76}$Sr$_{0.24}$CuO$_4$ | 20.0      | 2050                  | 6.6           | 106               |
| La$_{1.85}$Sr$_{0.15}$CuO$_4$ | 37.0      | 2400                  | 6.6           | 77                |
| La$_{1.9}$Sr$_{0.1}$CuO$_4$ | 30.0      | 3200                  | 6.6           | 44                |
| La$_{1.75}$Sr$_{0.25}$CuO$_4$ | 24.0      | 2800                  | 6.6           | 57                |
| $Y$Ba$_2$Cu$_3$O$_7$         | 92.5      | 1400                  | 4.29          | 148               |
| $Y$BaCuO(2\%Zn)              | 68.2      | 2600                  | 4.29          | 43                |
| $Y$BaCuO(3\%Zn)              | 55.0      | 3000                  | 4.29          | 32                |
| $Y$BaCuO(5\%Zn)              | 46.4      | 3700                  | 4.29          | 21                |
| $Y$Ba$_2$Cu$_3$O$_6.7$        | 66.0      | 2100                  | 4.29          | 66                |
| $Y$Ba$_2$Cu$_3$O$_6.57$       | 56.0      | 2900                  | 4.29          | 34                |
| $Y$Ba$_2$Cu$_3$O$_6.92$       | 91.5      | 1861                  | 4.29          | 84                |
| $Y$Ba$_2$Cu$_3$O$_6.88$       | 87.9      | 1864                  | 4.29          | 84                |
| $Y$Ba$_2$Cu$_3$O$_6.84$       | 87.0      | 1771                  | 4.29          | 92                |
| $Y$Ba$_2$Cu$_3$O$_6.79$       | 73.4      | 2156                  | 4.29          | 62                |
| $Y$Ba$_2$Cu$_3$O$_6.77$       | 67.9      | 2150                  | 4.29          | 63                |
| $Y$Ba$_2$Cu$_3$O$_6.74$       | 63.8      | 2022                  | 4.29          | 71                |
| $Y$Ba$_2$Cu$_3$O$_6.7$        | 60.0      | 2096                  | 4.29          | 66                |
| $Y$Ba$_2$Cu$_3$O$_6.65$       | 58.0      | 2035                  | 4.29          | 70                |
| $Y$Ba$_2$Cu$_3$O$_6.6$        | 56.0      | 2285                  | 4.29          | 56                |
| HgBa$_2$Cu$_4$O$_{4.49}$      | 70.0      | 2160                  | 9.5           | 138               |
| HgBa$_2$Cu$_4$O$_{4.55}$      | 78.2      | 1610                  | 9.5           | 248               |
| HgBa$_2$Cu$_4$O$_{4.65}$      | 78.5      | 2000                  | 9.5           | 161               |
| HgBa$_2$Cu$_4$O$_{4.66}$      | 88.5      | 1530                  | 9.5           | 274               |
| HgBa$_2$Cu$_4$O$_{4.96}$      | 95.6      | 1450                  | 9.5           | 305               |

$l > \xi(0)$, so that the parameter-free expression for $\epsilon_F$, Eq.(3), is perfectly applicable.

A parameter-free estimate of the Fermi energy obtained using Eq.(3) is presented in the Table. The renormalised Fermi energy of about 30 cuprates is less than 100 meV, in particular if the degeneracy $g \geq 2$ is taken into account. That should be compared with the characteristic phonon frequency, which is estimated as the plasma frequency of oxygen ions,

$$\omega_0 = \sqrt{\frac{4\pi Z^2 e^4 N}{M}}. \quad (4)$$

One obtains $\omega_0 = 84 meV$ with $Z = 2$, $N = 6/V_{cel}$, $M = 16 a.u.$ for $YBa_2Cu_3O_6$. Here $V_{cel}$ is the volume of the (chemical) unit cell. The estimate agrees with the measured phonon spectra. As established experimentally in cuprates, the high-frequency phonons are strongly coupled with carriers. Therefore the low Fermi energy is a serious problem for the BCS (or Migdal-Eliashberg) approach. Since the Fermi energy is small and phonon frequencies are high, the Coulomb pseudopotential $\mu^*_c$ is of the order of the bare Coulomb repulsion, $\mu^*_c \approx \mu_c \approx 1$ because the Tolmachev logarithm is ineffective. Hence, to get an experimental $T_c$, one has to have a strong coupling, $\lambda > \mu_c$. However, one cannot increase $\lambda$ without accounting for the polaron collapse of the band. Even in the region of the applicability of the Eliashberg theory (i.e. at $\lambda \lesssim 0.5$), the non-crossing diagrams cannot be treated as vertex corrections, since they are comparable to the standard terms, if $\omega_0/\epsilon_F \gtrsim 1$. Because novel superconductors are in the nonadiabatic regime, interaction with phonons must be treated in the framework of the multi-polaron theory at any value of $\lambda$.

In many cases (Table) the renormalized Fermi energy is so small that pairing is certainly individual, i.e. the bipolaron radius is smaller than the inter-carrier distance. Indeed, this is the case, if

$$\epsilon_F \lesssim \pi \Delta. \quad (5)$$

The bipolaron binding energy $\Delta$ is thought to be twice the so-called pseudogap experimentally measured in the normal state of many cuprates, $\Delta \gtrsim 100 meV$, so that Eq.(5) is well satisfied in underdoped and even in a few optimally and overdoped cuprates. One should notice that the coherence length in the charged Bose gas has nothing to do with the size of the boson. It depends on the interparticle distance and the mean-free path, $[10]$, and might be as large as in the BCS superconductor. Hence, it is incorrect to apply the ratio of the coherence length to the inter-carrier distance as a criterium of the BCS-Bose liquid crossover. The correct criterium is given by Eq.(5).

II. SYMMETRY OF THE ORDER PARAMETER

The anomalous Bogoliubov average

$$F_{ss'}(r_1, r_2) = \langle \langle \Psi_s(r_1)\Psi_{s'}(r_2) \rangle \rangle,$$

is the superconducting order parameter both in the weak and strong-coupling regimes ($\Psi_s(r)$ annihilates a carrier with spin $s$ and coordinate $r$). $F_{ss'}(r_1, r_2)$ depends on the relative coordinate $\rho = r_1 - r_2$ of two electrons of the pair, and on the center-of-mass coordinate $\mathbf{R} = (r_1 + r_2)/2$. Hence, its Fourier transform, $f(k, \mathbf{K})$, depends on the relative momentum $k$ and on the center-of-mass momentum $\mathbf{K}$. In the BCS theory, where $\mathbf{K} = 0$ (in a homogeneous superconductor), the Fourier transform of the order parameter is proportional to the gap in the quasiparticle excitation spectrum, $f(k, \mathbf{K}) \propto \Delta_k$. Hence the symmetry of the order parameter and the symmetry of the gap are the same in the weak-coupling regime. Under the rotation of the coordinate system, $\Delta_k$ changes its sign, if the Cooper pairing is d-wave. In this case the BCS quasiparticle spectrum is gapless.

In the bipolaron theory the symmetry of the Bose-Einstein condensate is not necessarily the same as the “internal” symmetry of a pair $[23]$. While the latter describes transformation of $f(k, \mathbf{K})$ with respect to the rotation of $k$, the former (“external”) symmetry is related
to the rotation of $\mathbf{K}$. Therefore it depends on the bipolaron band dispersion, but not on the symmetry of the bound state.

As an example, let us consider a tight-binding bipolaron spectrum comprising two bands on a square lattice with the period $a = 1$,

$$
E^x_K = t \cos(K_x) - t' \cos(K_y),
$$

$$
E^y_K = -t' \cos(K_x) + t \cos(K_y).
$$

They transform into one another under $\pi/2$ rotation. If $t,t' > 0$, "$x$" bipolaron band has its minima at $\mathbf{K} = (\pm \pi, 0)$ and $y$-band at $\mathbf{K} = (0, \pm \pi)$. These four states are degenerate, so that the condensate wave function $\psi_s(\mathbf{m})$ in the site space, $\mathbf{m} = (m_x, m_y)$, is given by

$$
\psi_s(\mathbf{m}) = N^{-1/2} \sum_{\mathbf{K} = (\pm \pi, 0), (0, \pm \pi)} b_{\mathbf{K}} e^{-i\mathbf{K} \cdot \mathbf{m}}.
$$

where $b_{\mathbf{K}} = \pm \sqrt{n_s}$ are $c$-numbers at $T = 0$. The superposition, Eq.(7), respects the time-reversal and parity symmetries, if

$$
\psi_s^\dagger(\mathbf{m}) = \sqrt{n_s} [\cos(\pi m_x) \pm \cos(\pi m_y)].
$$

Two order parameters, Eq.(8), are physically identical because they are related by the translation transformation, $\psi_s^\dagger(m_x, m_y) = \psi_s^\dagger(m_x, m_y + 1)$. Both have a $d$-wave symmetry changing sign, when the lattice is rotated by $\pi/2$, Fig.1. The $d$-wave symmetry is entirely due to the bipolaron energy dispersion with four minima at $\mathbf{K} \neq 0$. When the bipolaron spectrum is not degenerate and its minimum is located at $\Gamma$ point of the Brillouin zone, the condensate wave function is $s$-wave with respect to the center-of-mass coordinate. The symmetry of the normal state (pseudo)gap has little to do with the symmetry of the order parameter in the strong-coupling regime. The one-particle pseudogap is half of the bipolaron binding energy $\Delta/2$, and does not depend on any momentum in zero order of the polaron bandwidth, i.e. it has an "$s$"-wave symmetry. In fact, due to a finite dispersion of polaron and bipolaron bands, the pseudogap is an anisotropic $s$-wave. A multi-band electron structure can include bands weakly coupled with phonons which could overlap with the bipolaronic band. In this case CBG coexists with the Fermi gas, like $^4$He bosons co-exist with $^3$He fermions in the mixture of Helium-4 and Helium-3 \cite{10}. The normal state one-particle excitation spectrum of such mixtures is gapless.

### III. Checkerboard Modulations of the Superconducting Gap

Independent observations of normal state pseudogaps in a number of magnetic and kinetic measurements, and unusual critical phenomena tell us that many cuprates may not be BCS superconductors. Indeed their superconducting state is as anomalous as the normal one. In particular, there is strong evidence for a $d$-like order parameter (changing sign when the $CuO_2$ plane is rotated by $\pi/2$) in cuprates \cite{24}. A number of phase-sensitive experiments \cite{27} provide unambiguous evidence in this direction; furthermore, the low temperature magnetic penetration depth \cite{26,27} was found to be linear in a few cuprates as expected for a $d$-wave BCS superconductor. However, different tunnelling spectroscopies, in particular $c$-axis Josephson tunnelling \cite{28}, and some high-precision magnetic measurements \cite{29} show a more usual $s$-like symmetry. Other studies even reveal an upturn in the temperature dependence of the penetration depth below some characteristic temperature \cite{30}. Also both angle-resolved photoemission (ARPES) and tunnelling spectroscopies often show a very large energy gap with $2\Delta/T_c$ ratio well above that expected in any-coupling BCS theory.

Strong deviations from the Fermi/BCS-liquid behaviour are suggestive of a new electronic state in cuprates, which could be a charged Bose liquid of bipolarons. In the bipolaron theory the symmetry of the
Bose-Einstein condensate on a lattice should be distinguished from the ‘internal’ symmetry of a single-bipolaron wave function, and from the symmetry of a single-particle excitation gap. As described above the Bose-Einstein condensate of bipolarons could be d-wave, if bipolaron bands have their minima at finite \( \mathbf{K} \) in the center-of-mass Brillouin zone. At the same time the single-particle excitation spectrum is an anisotropic center-of-mass Brillouin zone. At the same time the experimental observations, suggesting an absence of in-plane carrier density modulation, is consistent with the inelastic neutron scattering to bipolaron band-minima. Such interpretation of stripes determined by inverse wave vectors correspond to bipolaron single-particle band-minima, as observed. Also recent X-ray spectroscopy \([31,32]\) did not find any bulk charge segregation in the normal state of a high-\(T_c\) La\(\text{CuO}_4\) cuprate, suggesting an absence of in-plane carrier density modulations in this material above \(T_c\).

The d-wave condensate reveals itself as a checkerboard real-space modulation of the hole density, Fig.1. Then the superconducting gap should be modulated as well. Indeed, as shown in Ref.\([37]\), the single-particle excitation spectrum of the bipolaronic superconductor can be obtained using the BCS excitation spectrum but with a negative chemical potential,

\[
\epsilon(\mathbf{k}) = \left[(k^2/2m^*) + \Delta_p^2 + \Delta_c(T)^2\right]^{1/2}, \tag{9}
\]

where \(\Delta_c(T)^2 = \text{constant} \times |\psi_n|^2\) is a coherent component of the gap. This spectrum is quite different from the BCS quasiparticles because the chemical potential is negative with respect to the bottom of the single-particle band, \(\mu = -\Delta_p^2\). A single particle gap, \(\Delta/2\), defined as the minimum of \(\epsilon(\mathbf{k})\), is given by

\[
\Delta/2 = \left[\Delta_p^2 + \Delta_c(T)^2\right]^{1/2}. \tag{10}
\]

It varies with temperature from \(\Delta(0)/2 = \left[\Delta_p^2 + \Delta_c(0)^2\right]^{1/2}\) at zero temperature down to the temperature independent \(\Delta_p^2\) above \(T_c\). The spectrum, Eq.(10) was obtained for a homogeneous condensate. However, in the framework of a semiclassical approximation, we can apply Eq.(10) also with a modulated \(\psi_n(\mathbf{m})\), if the period of modulations is large enough \([38]\). As a result, the superconducting gap is modulated. Importantly, the checkerboard modulation of the gap have been observed in the tunnelling experiments with \([39]\) and without \([40,41]\) applied magnetic field in \(\text{Bi}\) cuprates.

In conclusion, I have shown that there is a real-space pairing in many cuprates due to the polaron collapse of the Fermi energy. Remarkably, the bipolaron theory provides an explanation of the d-wave order parameter, the anisotropic s-wave single-particle gap, and its stripe checkerboard modulations below \(T_c\) within a single microscopic approach.

This work has been supported by the Leverhulme Trust (grant F/00261/H). I greatly appreciate enlightening discussions with I. Bozovic, K. McElroy, V. V. Kabanov, A. J. Leggett, D. Mihailovic, and K. A. Müller.

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